CENTRAL LIBRARY
Birla Institute of Technology & Science
PILANI (Rajasthan)

Call No. 540.3
T519
1937
Accession No. v.1
15337

Acc. No ...L5337...

ISSUE LABEL

Not later the latest date stamped below.

THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY
I

THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY

JOCELYN FIELD THORPE, C.B.E., D.Sc., F.R.S., F.I.C.

Professor of Organic Chemistry and Director of Organic Laboratories
Imperial College of Science and Technology. Past President
of the Chemical Society and of the Institute of
Chemistry

AND

M. A. WHITELEY, O.B.E., D.Sc., F.I.C.

Lately Assistant Professor of Organic Chemistry, Imperial
College of Science and Technology

ASSISTED BY EMINENT CONTRIBUTORS

FOURTH EDITION

WITH ILLUSTRATIONS

LONGMANS, GREEN AND CO.
LONDON ◆ NEW YORK ◆ TORONTO

LONGMANS, GREEN AND CO. LTD.
OF PATERNOSTER ROW
43 ALBERT DRIVE, LONDON, S.W. 19
NICOL ROAD, BOMBAY
17 CHITTARANJAN AVENUE, CALCUTTA
36A MOUNT ROAD, MADRAS

LONGMANS, GREEN AND CO.
55 FIFTH AVENUE, NEW YORK, 3

LONGMANS, GREEN AND CO.
215 VICTORIA STREET, TORONTO 1

FOURTH EDITION . . . . *June* 1937
REPRINTED BY NOVOGRAPHIC PROCESS *September* 1941
February 1943 *and April* 1945

CODE NUMBER: 96271

Printed in Great Britain by
Lowe & Brydone Printers Limited, London, N.W.10
All Rights Reserved

This edition of the Dictionary has been bound with material coloured with Monastral Fast Blue, BS. This pigment, which has been described as the greatest chemical achievement of 1936, *arose in a curious manner, which causes it to be particularly appropriate for use in the binding of a Dictionary of Applied Chemistry. It may be regarded as one of the few romances which underlie new discoveries in Chemical Science in its application to Industry.*

Scottish Dyes Ltd. found that many of their batches of phthalimide prepared from phthalic anhydride and ammonia by fusion in a porcelain-lined vessel were unsaleable owing to the presence in them of some blue stain. The origin of this stain was traced to a pinhole in the enamel, thus allowing the melt to come into contact with the iron of the vessel. The investigation of this impurity was placed in the hands of the Dyestuffs Group Research Committee of the I.C.I., and its constitution worked out for the Committee in the Organic Chemistry Laboratories of the Imperial College of Science and Technology. It appears that the constitution of the blue compound (phthalocyanine) *is similar to that of hæmin, the colouring matter of the blood, but has groups present which cause absorption in the red end of the spectrum* (*Linstead* et alia, *J.C.S.*, 1934, 1022). *As a matter of fact, it is a perfect blue, only a very small portion of the green of the spectrum entering into its colour composition. It shows properties in connection with fastness to light, acids, and alkalis which render it far above all other colours in these respects.*

FOREWORD.

THE final volume of the last edition of the Dictionary of Applied Chemistry inaugurated by the late Sir Edward Thorpe was published in 1927, and in their introduction to the first supplementary volume, issued in 1934, the present Editors stated that the advances which Chemical Science and its applications to Industry had made during the intervening period were so great that it had been agreed with the Publishers to issue the supplement in two volumes, the first containing the letters A to M, and the second those from N to Z. The second of these appeared in 1935, an Index and Glossary being added in 1936.

The supplementary volumes were designed to tide over a period during which a new edition of the complete work was being prepared. They were formed on a slightly modified plan, because it was realised that the best way to attack the problem involved was to bring the subjects up to date by means of articles which were essentially monographs; or, in other words, to deal with those sections in which the advances had been definite and distinct, by means of articles embracing the whole subject from its theoretical and laboratory initiation to its present-day industrial application.

The supplementary volumes can be regarded, therefore, as a record of the condition of the various subjects at the time of issue, written in a self-contained and readable manner. Apart, therefore, from their Dictionary value, they provide information which students of the subject will find instructive and of advantage in their studies and will, moreover, give the general enquirer a true picture of modern development.

It was clear, however, that in order to make the Dictionary serve the purpose for which it had been designed a new edition would have to be an entirely remodelled version of the last issue. It would be no longer possible to bring the existing edition up to date by means of patch-work additions which together with a certain number of new articles had sufficed in the case of the last edition. The Editors' advice to the Publishers was therefore to distribute the whole of the existing type and to start afresh with completely new matter. In effect this has been accomplished, although it has been found desirable to re-set the introductions to some of the articles from the last edition which it was considered should be retained not only on account of their historical value but because without them the articles would fail to provide the reading interest at which the Editors aimed.

As in the case of the supplementary volumes, the question of size became one of first importance. It was apparent that the new edition will have to be longer than the last edition if the various subjects are to be dealt with in a manner justified by the advances made during the period that has intervened since the last edition was published.

A comparison of the present volume with the corresponding volume in the last edition will show that experts have been asked to write the special articles dealing with their subjects. The Editors realise to the full that the day of the universalist is past and that the work in any special field must be described by an expert thoroughly acquainted with his subject. At the same time it has been remembered that specialists in branches of science other than Chemistry, as also in the Arts, frequently desire to know what is being accomplished in the development of subjects other than their own, and the Editors have done their best to ensure that the special articles are written in a manner which will be understood by the ordinarily cultured reader; nevertheless, in a subject so highly specialised as, for example, Organic Chemistry, this may not always have been achieved.

Those of us who have been privileged to live during the past forty years and who have had the knowledge to understand, as well as to appreciate, the vast progress both in Science and Industry that has been made, will realise that during no other period in the world's history has the increase of knowledge and its application to human requirements been greater or more rapid. Without doubt the War was responsible for much of this new knowledge, because each country found it necessary to supply itself and to manufacture many materials hitherto imported. Nevertheless, it would be untrue to make this a general statement, because it must be admitted that far greater advances have been made since the War ended than were made during the progress of the conflict. What the War demonstrated, and demonstrated in no uncertain manner, was the value of research and particularly that form of research which depends on team work for its progress. It showed that the lone scientific investigator, to whom was imparted the vision and inspiration of Science, could not usefully serve his fellow-men unless he had liaison with his brother scientist, the so-called technologist, whose business it was to apply knowledge thus acquired. The view that there was some essential difference between the theoretical and practical man, which rendered all communication between them impossible, was strongly held, and justly so, because in extreme cases the "practical" man and the "theorist" were widely separated, the former having his practical outlook strongly developed and the latter caring little whether his work were useful or not provided that his theoretical insight was satisfied. The War succeeded in doing that which in all probability many years of peace could not have accomplished, for it showed that the two types of mind could be made to work together and that few problems were insoluble if attacked by a team of resolute workers each providing his own power both of brain and of hand. It is, in all probability, to this cause that the chief advances made since the War are due.

It is perhaps to be deplored in some ways that this new method of scientific attack has been developed, because it is killing, and has in all probability in some cases already killed, that individuality upon which so much depends. A team-worker must be content to work for the cause and all question of personal credit must be set aside. Indeed, it is doubtful if such personal credit can be claimed, as in true team work all avenues of advance are explored after general discussion and the presence of a lone worker would be harmful to the work of the team as a whole. The claim, therefore, of being the sole inventor by any member of the team would be unfair to the team and could not properly be sustained. Whilst, however, there can be no question that team work is the best manner in which research can be prosecuted in Industry, there is more doubt about its applicability to Academic research. It is true that in the university work can be followed by utilising the team plan, but in this case the method used in Industry must be modified so as to place in the forefront the work of the school, each member of which should be assigned some section, self-contained wherever possible, in order that he may exercise his individuality of thought and at the same time add to the amount of knowledge required for the progress of the school as a whole. In this way he will not only retain his own individuality but will learn the discipline required to make him a member of a team working in Industry.

The new edition of the Dictionary has been planned so as to embody the monographical aspect present in the supplementary volumes as well as the Dictionary style of the previous edition. It is intended to publish one volume yearly, the last volume containing a General Index and Glossary. The publication of the work over a prolonged period means that a slightly modified system has had to be introduced so as to avoid giving in the earlier volumes reference to volumes which may not appear for some years. In order to ensure this, each volume will be used as a means of bringing a previous volume up to date. Thus each item of importance contained in a general article in an earlier volume will be dealt with in a later volume under its own initial letter, and any up-to-date additions included. In a similar manner earlier volumes will contain items of importance dealt with in general articles in later volumes, and in this case such items will be brought up to date in the later volume.

To give an illustration: (1) Material having the initial letter *A* is described as part of a general article under say the letter *O*. It will be described under the initial letter *A* and any new matter will be added when the volume containing the letter *O* is published. (2) A material having the initial letter *H* is described in a general article under *B*. It will be again mentioned in the volume containing the letter *H* and any new information added.

We have again to thank Dr. J. N. Goldsmith who, despite serious ill health, has been able to render us valuable assistance. We have also to thank the Printers, who have so admirably set up the complex formulæ. Nevertheless, the formulæ in the first volume, especially those dealing with derivatives of benzene, must not be regarded as having been drawn to scale, that is to say they do not represent in any way the relative distances apart of the atoms composing them as shown by X-ray analysis. It is hoped that in later volumes this important factor will be introduced.

We have also to thank those publishers and authors who have granted us permission to use extracts from their works for the purpose of the Dictionary, as well as the Pharmaceutical Society of Great Britain for permission to quote from the British Pharmaceutical Codex, 1934. It will be noticed that in every case suitable acknowledgment is made in the appropriate place.

J. F. THORPE
M. A. WHITELEY

South Kensington,
April, 1937.

LIST OF CONTRIBUTORS

TO VOLUME I.

ANDERSON, J. S., Ph.D., A.R.C.S., *Assistant Lecturer, Imperial College of Science and Technology, S.W.7.* [Azoimide.]

E. FRANKLAND ARMSTRONG, Ph.D., D.Sc., LL.D., F.R.S. [Acacin; α- and β-Acrose; Adonitol; Æsculin; Alizarin Glycosides; Allolactose; Allose; Aloins; Altrose; Amygdalin; α- and β-Amylans; Amylase; Androsin; Antiarin; Apiin; Apiose; Arabinose; Arabitol; Arbutin; Arginase; Asparaginase; Aspartase; Asperulin; Aucubin; Baicalin; Baptisin; Betitol.]

G. L. BAILEY, M.Sc., *Development Officer, British Non-Ferrous Metals Research Association.* [Annealing.]

WILSON BAKER, M.A.(Oxon), D.Sc.(Manchester), *University Demonstrator in Chemistry, The Dyson Perrins Laboratory, Oxford.* [Amines.]

C. O. BANNISTER, M.Eng., A.R.S.M., *Professor of Metallurgy, University of Liverpool.* [Antimony; Bismuth.]

C. O. BANNISTER and J. N. GOLDSMITH. [Arsenic.]

G. BARGER, (Hon.)D.Sc., (Hon.)M.D., LL.D., F.R.S., *Professor of Medical Chemistry, University of Edinburgh.* [Aconitine and the Aconite Alkaloids; Aloes or Bitter Aloes; Alstonia Bark; Ambaline; Ammodendrine; Anabasine; Aporeine; Arbotrine; Areca Nut; Aribine; Aristolochine; Artabotrine; Bebeerine; Betaines.]

G. BARGER and F. L. PYMAN. [Alkaloids.]

Professor B. T. P. BARKER, M.A., *Director of the Long Ashton Research Station, University of Bristol.* [Apple Pulp.]

CHARLES THOMAS BENNETT, B.Sc.(Lond.), F.I.C. *Chief Chemist to Wright, Layman and Umney, Ltd., 46 Southwark Street, S.E.1. Formerly Lecturer on the Chemistry of Essential Oils at the Borough Polytechnic Institute, S.E.1.* [Ajowan Oil; Aloes Wood; Alpinia Oil; Anise Oil; Asarum Canadense; Attar of Roses; Birch-Bark Oil; Essential Oils of :—Absinth; Acorus Calamus; Almond Oil; Amber; Angelica; Basil; Bay; Bergamot.]

LAURENCE R. BISHOP, M.A., Ph.D., *Institute of Brewing Research Laboratories, the University, Edgbaston, Birmingham.* [Barley.]

G. S. BLAKE, A.R.S.M., M.I.M.M., B.Sc., F.G.S., *Geological Adviser, Palestine Government.* [Barium.]

G. F. BLOOMFIELD, Ph.D., D.I.C., A.R.C.S., A.I.C., *Research Chemist, The British Xylonite Co., Ltd.* [Adipic Acid; Arachidic Acid; Azelaic Acid; Behenic Acid.]

D. BRUNT, M.A., B.Sc., *Professor of Meteorology, Imperial College of Science and Technology, S.W.7.* [Atmosphere.]

J. L. BUCHAN, M.Sc., A.I.C., *Chemist, Government Laboratory, W.C.2.* [Balance, The Conrady's Method of Weighing.]

M. CARLTON, B.Sc., Ph.D., D.I.C., *Imperial College of Science and Technology, S.W.7.* [Actinium; Atomic Data of the Elements.]

FREDERICK CHALLENGER, B.Sc.(Lond.), Ph.D.(Göttingen), D.Sc.(Birmingham), F.I.C., *Professor of Organic Chemistry, University of Leeds.* [Bismuth, Organic Compounds of.]

C. W. DANNATT, A.R.S.M., D.I.C., F.I.C., *Lecturer in Assaying and Metallurgical Analysis, Royal School of Mines, S.W.7.* [Assaying.]

J. N. E. DAY, M.Sc., Ph.D., D.I.C., A.R.C.S., A.I.C., *Lecturer in Chemistry, University College, London.* [Acetoacetic Acids ; Acetopropionic Acid ; Aldehydes.]

A. E. DUNSTAN, D.Sc., F.I.C., *Chief Chemist, Anglo-Iranian Oil Co., Britannic House, E.C.2.* [Acids from the Oxidation of Petroleum ; Alcohols for Motor Fuels ; Alcohols produced by Synthesis from Petroleum ; Aromatic Hydrocarbons in Petroleum ; Bauxite as a Refining Agent.]

H. J. EMELÉUS, D.Sc., A.R.C.S., *Lecturer in Chemistry, Imperial College of Science and Technology, S.W.7.* [Argon ; Atomic Structure.]

E. V. EVANS, O.B.E., F.I.C., *South Metropolitan Gas Company.* [Anthracene ; Benzene and its Homologues.]

D. M. FAIRLIE, M.Sc., *Research Chemist, British Aluminium Co., Ltd., Kinlochleven.* [Aluminium, Metallurgy of.]

E. H. FARMER, D.Sc., F.I.C., *Lecturer in Organic Chemistry, Imperial College of Science and Technology, S.W.7.* [Acetylenes ; Allenes ; Amylene.]

M. L. V. GAYLER, D.Sc.(Lond.), *Scientific Officer, National Physical Laboratory, Teddington.* [Amalgam.]

ALAN A. GOLDBERG, Ph.D., D.Sc.(Lond.), D.I.C., A.I.C., *Chief Chemist at Messrs. James R. Crompton & Bros., Ltd., Elton Paper Mills, Bury ; and Head of Chemical Dept., Bolton Technical College, Bolton.* [Anthranol ; Anthraquinone.]

J. N. GOLDSMITH, Ph.D., F.I.C., *Consulting Chemist.* [Abies ; Abrus Precatorius ; Accelerators ; Acorus Calamus ; Aerosols ; Agave ; Alder Bark ; Aleurites species ; Bird Lime.]

ARTHUR G. GREEN, F.I.C., F.R.S., *Late Director of Research, British Dyestuffs Corporation, and formerly Professor of Colour Chemistry, University of Leeds.* [Acetate Silk Dyes.]

HUGH GRIFFITHS, B.Sc., A.R.C.S., M.I.Chem.E., *Director, British Carbo Union, Ltd.* [Adsorption.]

Professor J. M. GULLAND, M.A., D.Sc., Ph.D., *Sir Jesse Boot Professor of Chemistry, University College, Nottingham.* [Amino Acids.]

W. C. HANCOCK, B.A., F.I.C., *Lecturer in Refractory Materials and Silicate Technology, Imperial College of Science and Technology, S.W.7.* [Alundum.]

LESLIE J. HARRIS, Ph.D., Sc.D.(Cantab.), D.Sc.(Manchester), *Director of Nutritional Laboratory, University of Cambridge and Medical Research Council.* [Aneurin ; *l*-Ascorbic Acid ; B_1 Vitamin ; Bios.]

I. M. HEILBRON, D.S.O., D.Sc.(Glasgow), Ph.D.(Leipzig), F.I.C., F.R.S., *Sir Samuel Hall Professor of Chemistry and Director of the Chemical Laboratories, Manchester University,* and R. F. PHIPERS, B.Sc., Ph.D., *Chemist, Messrs. Cooper, McDougall and Robertson, Ltd., Berkhamstead.* [Actinioerythrin ; Agar-Agar ; Algæ ; Alginic Acid ; Annatto ; Antheraxanthin ; Astacin ; Asteric Acid ; Azafrin.]

JOHN THEODORE HEWITT, A.R.C.S., M.A., Ph.D., D.Sc., F.R.S., *Emeritus Professor of Chemistry, Queen Mary College.* [Acridine.]

H. HOLLINGS, M.Sc., *Chief Gas Chemist to the Gas Light and Coke Co.,* and L. SILVER, A.R.C.S., B.Sc., *Gas Light and Coke Co.* [Absorption.]

FREEMAN HORN, *Intelligence Officer, British Aluminium Co., Ltd.* [Alloys, Light.]

LOUIS ARNOLD JORDAN, D.Sc., A.R.C.S., D.I.C., F.I.C., M.I.Ch.E., *Director, Research Association of British Paint, Colour and Varnish Manufacturers, The Paint Research Station, Teddington.* [Ageing, Accelerated.]

D. W. KENT-JONES, Ph.D., B.Sc., F.I.C., *Analytical and Consulting Chemist, The Laboratories, Charlton Green, Dover.* [Baking Powders.]

J. C. KERNOT, F.I.C., *Adhesives Research Committee, Department of Scientific and Industrial Research.* [Adhesives.]

G. A. R. KON, M.A., D.Sc., *Assistant Professor of Organic Chemistry, Imperial College of Science and Technology, S.W.7.* [Androsterone.]

P. R. ELSA LEWKOWITSCH, Ph.D., D.I.C., *Lewkowitsch Laboratory, 71 Priory Road, N.W.6.* [ACETIN; ACORN OIL; ADIPOCERE; ALMOND OIL; ANACARDIUM NUT; ARACHIS OIL; ARGAN OIL; AVOCADO OIL; BASSIA FATS; BASSWOOD OIL; BEECHNUT OIL; BEN OIL.]

R. P. LINSTEAD, D.Sc., Ph.D., D.I.C., A.R.C.S., *Lecturer in Organic Chemistry, Imperial College of Science and Technology, S.W.7.* [AURAMINE.]

JOHN J. MANLEY, M.A., D.Sc.(Oxon), *Fellow of Magdalen College, Oxford.* [BALANCE.]

FREDERICK A. MASON, M.A., Ph.D., F.I.C., *formerly Lecturer in Dyestuffs and Tinctorial Chemistry, College of Technology, Manchester.* [ACETALDEHYDE; ACETALS; ACETYLENE; AZINES.]

C. AINSWORTH MITCHELL, M.A., D.Sc.(Oxon), F.I.C., *Consulting Chemist, Editor of "The Analyst."* [ACETIC ACID; AERATED OR MINERAL WATERS.]

Sir GILBERT T. MORGAN, O.B.E., D.Sc.(Lond.), Sc.D.(Dublin), LL.D.(Birmingham), A.R.C.Sc., F.I.C., F.R.S., *Director of Chemical Research, Department of Scientific and Industrial Research, Chemical Research Laboratory, Teddington, Middlesex.* [AUTOCLAVES.]

Sir GILBERT T. MORGAN and GLYN REES DAVIES, Ph.D.(Birmingham), B.Sc.(Lond.), *Research Chemist, Chemical Research Laboratory, Teddington, Middlesex.* [ANTIMONIALS, ORGANIC; ARSENICALS, ORGANIC.]

D. M. NEWITT, D.Sc., *Assistant Professor of Chemical Technology, the Imperial College of Science and Technology, S.W.7.* [AUTOCLAVES FOR HIGH PRESSURES AND LIQUID PHASE REACTIONS.]

E. G. NOBLE, Ph.D., A.I.C., *Chemist, Nobel Chemical Finishes, Ltd., Slough, Bucks.* [ALLYL; AMYL.]

J. R. PARK, M.Sc., *Research Chemist, Imperial Chemical Industries (Fertiliser and Synthetic Products), Ltd., Billingham, Co. Durham.* [AMMONIA.]

ERNEST J. PARRY, D.Sc.(Lond.), F.I.C., *Barrister-at-Law.* [ACACIA GUM; ACETONAPHTHONE; AMBER, CONSTITUTION OF; AMBERGRIS; AMBREIN; AMMONIACUM; AMYL ESTERS; α-AMYLCINNAMALDEHYDE; ANISALDEHYDE; ASAFŒTIDA; BALSAMS; BDELLIUM; BENZALDEHYDE, USE OF IN SYNTHETIC PERFUMES; BENZOPHENONE; BENZYL ESTERS; BENZYLIDENE ACETONE.]

T. G. PEARSON, M.Sc., Ph.D., *Imperial College of Science and Technology, S.W.7.* [ALUMINIUM, COMPOUNDS OF.]

Emeritus Professor A. G. PERKIN, D.Sc., F.I.C., F.R.S.E., F.R.S., *University of Leeds,* and E. J. CROSS, Ph.D., *Lecturer in Colour Chemistry, University of Leeds.* [ADSUKI BEAN; AFRICAN MARIGOLD; ALGARROBIN; ALKANET; ASBARG; AWOBANA; BARBATIC ACID; BARBERRY; BARWOOD; BIGNONIA TECOMA.]

A. G. POLLARD, B.Sc., A.R.C.S., D.I.C., *Lecturer in Agricultural Chemistry, Imperial College of Science and Technology, S.W.7.* [ALEURONE GRAINS; ALMOND; APRICOT; ARROWROOT; ARTICHOKE; ASPARAGUS; AUXIN; AVOCADO PEAR; BANANA; BATATAS; BEAN; BEET; BILBERRY.]

JOHN PRYDE, D.Sc., *Lecturer in Physiological Chemistry, Physiology Institute, Newport Road, Cardiff.* [BILE.]

R. H. PURCELL, Ph.D., D.I.C., A.R.C.S., *Assistant Lecturer in Physical Chemistry, Imperial College of Science and Technology, S.W.7.* [ALLOTROPY.]

F. L. PYMAN, Ph.D., D.Sc., F.I.C., F.R.S., *Director of Research, Boots Pure Drug Co., Ltd., Nottingham.* [BERBERINE.]

J. H. QUASTEL, D.Sc., F.I.C., *Director of Research, Cardiff City Mental Hospital.* [AUTOLYSIS; BILE PIGMENTS.]

DEREK RICHTER, M.A., B.Sc.(Oxon), Ph.D.(Munich), *Assistant Demonstrator, Biochemical Laboratory, Tennis Court Road, Cambridge.* [ALIZARIN AND ALLIED DYESTUFFS.]

W. A. ROACH, D.Sc., A.R.C.S., D.I.C., A.I.C., *Head of Biochemical Section, East Malling Research Station, Kent.* [APPLE; ASH.]

S. W. ROWELL, B.A., D.Phil., *Imperial Chemical Industries, Ltd.* [ACETYLENE, CHLORINE DERIVATIVES OF.]

ROSE SCOTT-MONCRIEFF, Ph.D., B.Sc., A.R.C.S., *Biochemist, John Innes Horticultural Institution, S.W.*19. [Althein; Ampelopsin; Anthocyans; Antirrhinin; Asterin; Betanin.]

W. A. SEXTON, Ph.D., B.Sc., F.I.C., *Research Chemist, Imperial Chemical Industries (Dyestuffs Group), Blackley, Manchester.* [Aniline; Benzene, Derivatives of and its Homologues.]

H. SHANKSTER, F.I.C., *Department of the War Department Chemist, Woolwich Arsenal.* [Abelite; Akardit; Alumatol; Amatol; Amatoxol; Amberite; Amide Powder; Ammonal; Ammonium Nitrate, as a Constituent of Explosives; Ammonpulver; Astralit; Azides; Ballistite; Baratol.]

Professor J. L. SIMONSEN, D.Sc., F.I.C., F.R.S., *University College of North Wales, Bangor.* [Aromadendrene; Ascaridole; Atlantone; Betulol; Bisabolene.]

L. J. SPENCER, C.B.E., M.A., Sc.D., F.R.S., *Formerly Keeper of Minerals, British Museum.* [Abrasives; Adamite; Æschynite; Afridol; Agalite; Agalmatolite; Agate; Akrochordite; Alabaster; Alaite; Alamosite; Allanite; Allodelphite; Alstonite; Alum-Shale; Alunite or Alum Stone; Alunogen; Amarillite; Amazonite or Amazon Stone; Amber or Succinite; Amblygonite; Amethyst; Ampangabeite; Anabasine; Anatase; Ancylite; Andalusite; Andesine; Andesite; Andorite; Anglesite; Anhydrite; Ankerite; Apatite; Aphthitalite; Aragonite; Aramayoite; Arandisite; Ardennite; Argentite; Argyrodite; Arsenoklasite; Asbestos; Atacamite; Augelite; Aurosmirid; Austinite; Autunite or Calco-Uranite; Avogadrite; Axinite; Azurite; Baddeleyite; Baeumlerite; Bakerite; Barylite; Baryte; Barytocalcite; Basalt; Bastnäsite; Bauxite; Bavenite; Beckelite; Becquerelite; Beidellite; Bellite; Benitoite; Bentonite; Bertrandite; Beryl; Beryllonite; Berzelianite; Berzeliite; Betafite; Bismite or Bismuth Ochre; Bismoclite; Bismuthinite or Bismuth Glance; Bismutite; Bismutotantalite.]

F. S. SPRING, B.Sc., Ph.D., *Lecturer in Chemistry, The University, Manchester.* [Æscigenin; Agathic Acid; α- and β-Amyrins; Betulin.]

E. STEDMAN, Ph.D., D.Sc., *Lecturer in Medical Chemistry, University of Edinburgh.* [Anæsthetics.]

A. STEPHENSON, M.I.Mech.E., *Chief of the Dissolved Acetylene Technical Dept., The British Oxygen Co., Ltd., Thames House, Millbank, Westminster, S.W.*1. and N. DANIEL, B.Sc., A.I.C., *The British Oxygen Company, Ltd.* [Acetylene, Its Use in Industry.]

F. G. H. TATE, F.I.C., *Superintending Chemist, Government Laboratory, London.* [Absinth; Absinthin; Absinthol; Alcohol; Alcoholometry; Aniseed; Arrack; Bakhar; Bassia Mahwa or Mowrah Flowers.]

Dr. R. FRASER THOMSON, M.A., *Imperial Chemical Industries (Dyestuffs Group), Ltd.* [Anthraquinone Dyestuffs.]

W. V. THORPE, M.A., Ph.D., *Reader in Chemical Physiology, University of Birmingham.* [Anserine; Arcaine.]

E. E. WALKER, D.Sc.(Lond.), D.I.C., A.C.G.I. [Ameroid; Bakelite; Beetle; Bituminous Plastics.]

M. A. WHITELEY, O.B.E., D.Sc., F.I.C., *formerly Assistant Professor of Organic Chemistry, Imperial College of Science and Technology, S.W.*7. [Acetol; Alloxan; Alloxantin; Barbituric Acid.]

M. A. WHITELEY and W. V. THORPE. [Adenine; Alanine; Allantoin; Arginine; Asparagine; Aspartic Acid.]

DONALD M. WILSON, M.C., B.Sc., A.I.C., *Chief Chemist, D. Anderson & Son, Ltd., Park Road Works, Stretford, Manchester.* [Albertite; Asphalt-Bitumen.]

ABBREVIATIONS

OF THE TITLES OF JOURNALS, ETC.

(Reproduced by permission of the Bureau of Abstracts.)

A. I ; *A.* II ; *A.* III	British Chemical Abstracts.—A. Pure Chemistry.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Acta Bot. Fennica	Acta Botanica Fennica.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicæ	Acta Societatis Scientiarum Fennicæ.
Agric. Eng.	Agricultural Engineering.
Agric. Gaz. New South Wales	Agricultural Gazette of New South Wales.
Agric. J. Brit. Guiana	Agricultural Journal of British Guiana.
Agric. Live-stock India	Agriculture and Live-stock in India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Reports and Bulletins.
Allgem. Oel- Fett-Ztg.	Allgemeine Oel- und Fett-Zeitung.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Aluminium	Aluminium.
Amer. Chem. Abstr.	Chemical Abstracts. Published by the American Chemical Society.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. Gas J.	American Gas Journal.
Amer. Inst. Min. Met. Eng. Publ.	American Institute of Mining and Metallurgical Engineers Publication.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health and the Nation's Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Ink Maker	American Ink Maker.
Amer. Paint J.	American Paint Journal.
Amer. Potato J.	American Potato Journal.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Anal. Inst. invest. cient. tecn.	Anales del Instituto de investigaciones científicas y tecnológicas.
Analyst	Analyst.
Anat. Rec.	Anatomical Record.
Angew. Bot.	Angewandte Botanik.
Angew. Chem.	Angewandte Chemie (changed from Z. angew. Chem. in 1932).
Anilinokras. Prom.	Anilinokrasotschnaja Promischlennosti.
Ann. Acad. Brasil. Sci.	Annals da Academia Brasileira de Sciencias.
Ann. Acad. Sci. Fennicæ	Annales Academiæ Scientiarum Fennicæ.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomique.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. di Bot.	Annali di Botanica.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Ann. Falsif.	Annales des Falsifications.
Ann. Guébhard-Séverine	Annales Guébhard-Séverine.
Ann. Inst. Anal. Phys. Chim.	Annales de l'Institut d'Analyse Physico-chimique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Mines Belg.	Annales des Mines de Belgique.

Ann. Inst. Platine	*Title changed* to Ann. Sect. Platine.
Ann. Off. nat. Comb. liq.	Annales de l'Office nationale des Combustibles liquides.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. Sect. Platine	Annales du Secteur Platine et des autres Métaux Précieux.
Ann. Soc. Sci. Bruxelles	Annales de la Société Scientifique de Bruxelles.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Apoth.-Ztg.	Apotheker-Zeitung.
Arb. Biol. Reichanst. Land- u. Forstwirts.	Arbeiten der Biologisches Reichanstalt fur Land- und Forstwirtschaft.
Arch. Biol.	Archives de Biologie.
Arch. Eisenhüttenw.	Archiv. für das Eisenhüttenwesen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Gewerbepath. Gewerbehyg.	Archiv für Gewerbepathologie und Gewerbehygiene.
Arch. Hyg. Bakt.	Archiv der Hygiene und Bakteriologie.
Arch. Int. Med.	Archives of Internal Medicine.
Arch. Ist. Biochim. Ital.	Archivio dello Istituto Biochimico Italiano.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Min. Soc. Sci. Varsovie	Archives de Minéralogie de la Société des Sciences de Varsovie (Archivum Mineralogiczne Towarzystwa Naukowego Warszawskiego).
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. Physiol.	Archives Néerlandaises de Physiologie de l'Homme et des Animaux.
Arch. Pflanzenbau	Archiv. für Pflanzenbau.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Protistenk.	Archiv für Protistenkunde.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië..
Arch. Tierernährung u. Tierzucht	Archiv für Tierernährung und Tierzucht.
Arch. Wärmewirts.	Archiv für Wärmewirtschaft.
Arh. Hemiju	Arhiv za Hemiju i Farmaciju.
Arizona Agric. Exp. Sta. Bull.	Arizona Agricultural Experiment Station Bulletin.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Arxius	Arxius de l'Escola Superior d'Agricultura, Catalunya.
Astrophys. J.	Astrophysics Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts. B.—Applied Chemistry.
B.P.	British Patent.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Ges. Kohlentech.	Berichte der Gesellschaft für Kohlentechnik.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. Ukrain. Wiss. Forsch. physikal. Chem.	Berichte des Ukrainischen Wissenschaftlichen Forschungsinstituts für physikalische Chemie.
Berlin. klin. Woch.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Bied. Zentr. (Tierernähr.)	Biedermann's Zentralblatt (Tierernährung).
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biochimia	Biochimia.
Board Greenkeeping Res. J.	Board of Greenkeeping Research Journal.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacional dos Ciencias, Cordoba.
Bol. Soc. Quim. Peru	Boletin de la Sociedad Quimica del Peru.
Boll. Chim. farm.	Bollettino Chimico-Farmaceutico.
Boll. Sez. Ital.	Bolletino della Sezione Italiana.
Boll. Soc. Geol. Ital.	Bollettino della Società Geologica Italiana.
Boll. Soc. Ital. Biol. sperim.	Bolletino della Società Italiana di Biologia sperimentalla.

Boll. Soc. Med.-Chirurg.	Bollettino della Società Medico-Chirurgica, Pavia.
Boll. Staz. Sperim. Ind. Carta Fibre Tess.	Bollettino del Reparto Fibre Tessili Vegetali della R. Stazione Sperimentale per le Industrie della Carta e delle Fibre Tessili Vegetali.
Boll. Uff. Staz. Sperim. Ind. Essenze	Bollettino Ufficiale della R. Stazione Sperimentale per l'Industria delle Essenze e dei Derivati dagli Agrumi in Reggio Calabria.
Boll. Uff. Staz. Sperim. Ind. Pelli	R. Stazione Sperimentale per l'Industria delle Pelli e delle materie concianti, Bollettino Ufficiale.
Bot. Archiv	Botanisches Archiv.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Braunkohlenarchiv	Braunkohlenarchiv.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. Guiana Dept. Agric. Bull.	British Guiana Department of Agriculture Bulletin.
Brit. J. Phot.	British Journal of Photography.
Brit. J. Phys. Med.	British Journal of Physical Medicine.
Brit. Med. J.	British Medical Journal.
Brit. Plastics	British Plastics and Moulded Products Trader.
Bul. Chim.	Buletinul Chimie.
Bul. Chim. Soc. Române	Buletinul de Chimie pura si aplicata al Societatii Române de Chimie.
Bul. Soc. Chim. România	Buletinul Societătii de Chimie din România.
Bul. Soc. Fiz. România	Buletinul Bilunar al Societătii de Fizică din România.
Bul. Soc. Române Stiin.	Buletinul Societatii Române de Stiinte.
Bull. Acad. Méd. Roumanie	Bulletin de l'Académie de Médecine de Roumanie.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Agra & Oudh	Bulletin of the Academy of Sciences of Agra and Oudh.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Sociétiques Socialistes.
Bull. Agric. Chem. Soc. Japan	Bulletin of the Agricultural Chemical Society of Japan.
Bull. Amer. Ceram. Soc	Bulletin of the American Ceramic Society.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Dept. Agric. Kenya	Bulletin of the Department of Agriculture of Kenya.
Bull. Dept. Agric. of South Africa	Bulletin of the Department of Agriculture of South Africa.
Bull. Entomol. Res.	Bulletin of Entomological Research.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikagaku Kenkyujo Ihō).
Bull. Inst. Pin	Bulletin de l'Institut du Pin.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Math. Phys. Bucarest	Bulletin de Mathématiques et de Physique pure et appliquées de l'Ecole Polytechnique " Roi Carol II " Bucarest.
Bull. Mat. Grasses	Bulletin des Matières Grasses.
Bull. Photogrammétrie	Bulletin de Photogrammétrie.
Bull. School Mines and Met., Univ. Missouri.	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Sericult. Japan	Bulletin of Sericulture and Silk Industry, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Chim. Yougoslav.	Bulletin de la Société Chimique du Royaume de Yougoslavie.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. Franç. Min.	Bulletin de la Société Française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie et de Cinématographie.

Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Canad. Dairy & Ice Cream J.	Canadian Dairy and Ice Cream Journal.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
Canad. Chem. Met.	Canadian Chemistry and Metallurgy.
Canad. J. Res.	Canadian Journal of Research.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cellulosechem.	Cellulosechemie.
Cement and Lime Manuf.	Cement and Lime Manufacture.
Cereal Chem.	Cereal Chemistry.
Chaleur et Ind.	Chaleur et Industrie.
Ch. Abs.	Chemical Abstracts.
Chem. Age	Chemical Age.
Chem. App.	Chemische Apparatur.
Chem. Eng. Min. Rev.	Chemical Engineering and Mining Review.
Chem. Erde	Chemie der Erde.
Chem. Fabr.	Die Chemische Fabrik.
Chem. and Ind.	Chemistry and Industry.
Chem. Ind.	Chemische Industrie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vedu a Průmysl."
Chem. Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Social. Agric.	Chemisation of Socialistic Agriculture (U.S.S.R.).
Chem. Trade J.	Chemical Trade Journal.
Chem. Weekblad	Chemisch Weekblad.
Chem.-Ztg.	Chemiker-Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Cheshunt Agric. Exp. Sta. Ann. Rep.	Cheshunt Agricultural Experiment Station Annual Reports.
Chim. e l'Ind.	La Chimica e l'Industria.
Chim. et Ind.	Chimie et Industrie.
Chinese Med. J.	Chinese Medical Journal.
Chinese J. Physics.	Chinese Journal of Physics.
Chinese J. Physiol.	Chinese Journal of Physiology.
Coal Carbonisation	Coal Carbonisation.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemica Communications.
Collegium	Collegium.
Coll. Eng.	Colliery Engineering.
Coll. Guard.	Colliery Guardian.
Colorado Agric. Exp. Sta. Bull.	Colorado Agricultural Experiment Station Bulletin.
Combustion	Combustion.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Contr. Boyce Thompson Inst.	Contributions from Boyce Thompson Institute.
Cornell Univ. Agric. Exp. Sta. Bull.	Cornell University Agricultural Experiment Station Bulletin.
Current Sci.	Current Science.
Cyprus Agric. J.	Cyprus Agricultural Journal.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Delaware Agric. Exp. Sta. Bull.	Delaware Agricultural Experiment Station Bulletin.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
East Malling Res. Sta., Ann. Repts., etc.	East Malling Research Station, Annual Reports, etc.
Ecology	Ecology.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Empire Cotton Growing Rev.	Empire Cotton Growing Review.
Empire Cotton Growing Rep. Exp. Sta.	Empire Cotton Growing Reports of the Experimental Station.

Empire J. Exp. Agric.	Empire Journal of Experimental Agriculture.
Endocrinol.	Endocrinology.
Engineer	Engineer.
Engineering	Engineering.
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News-Rec.	Engineering News-Record.
Enzymologia	Enzymologia.
Ernährung	Die Ernährung.
Ernähr. Pflanze	Ernährung der Pflanze.
F.P.	French Patent.
Facts about Sugar	Facts about Sugar.
Farbe u. Lack	Farbe und Lack.
Farben-Chem.	Farben-Chemiker.
Farben-Ztg.	Farben-Zeitung.
Farve og Lak	Farve og Lak.
Fermentforsch.	Fermentforschung.
Fert. Feeding Stuffs J.	Fertiliser, Feeding Stuffs and Farm Supplies Journal.
Fette u. Seifen	Fette und Seifen.
Feuerfest	Feuerfest.
Feuerungstech.	Feuerungstechnik.
Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Flora	Flora.
Florida Agric. Exp. Sta. Bull.	Florida Agricultural Experiment Station Bulletin.
Food	Food.
Food Manuf.	Food Manufacture.
Food Res.	Food Research.
Forstarchiv	Forstarchiv.
Foundry Trade J.	Foundry Trade Journal.
Fruit Prod. J.	Fruit Products Journal.
Fuel	Fuel in Science and Practice.
Fuel Econ.	Fuel Economist.
Fuel Econ. Rev.	Fuel Economy Review.
G.P.	German Patent.
Gas Ind.	Gas Industry.
Gas J.	Gas Journal.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gas World	Gas World.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Georgia Agric. Exp. Sta. Bull.	Georgia Agricultural Experiment Station Bulletin.
Ges. Abh. Kennt. Kohle	Gesammelte Abhandlungen der Kenntnis der Kohle.
Glückauf	Glückauf.
Gummi-Ztg.	Gummi-Zeitung.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hilgardia	Hilgardia.
Hosiery Tr. J.	Hosiery Trade Journal.
Imp. Bur. Soil Sci. Tech. Comm.	Imperial Bureau of Soil Science, Technical Communications.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
Indian J. Vet. Sci.	Indian Journal of Veterinary Science.
Indian Lac Res. Inst. Bull.	Indian Lac Research Institute Bulletin.
India-rubber J.	India-rubber Journal.
Ind. Chem.	Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry, Analytical Edition.
Int. Rev. Agric.	International Review of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S.	Journal of the Chemical Society.
Jahrb. geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.

Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Japan. J. Med. Sci.	Japanese Journal of Medical Sciences.
Japan. J. Physics	Japanese Journal of Physics.
Japan Nickel Rev.	Japan Nickel Review.
Jernk. Ann.	Jern-kontorets Annaler.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Soc. Mech. Eng.	Journal of the American Society of Mechanical Engineers.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Annamalai Univ.	Journal of the Annamalai University.
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Austral. Inst. Agric. Sci.	Journal of the Australian Institute of Agricultural Science.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Brit. Dairy Farmers' Assoc.	Journal of the British Dairy Farmers' Association.
J. Brit. Wood Pres. Assoc.	Journal of the British Wood Preserving Association.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Cancer Res. Comm. Sydney.	Journal of the Cancer Research Committee of the University of Sydney.
J. Cell. Comp. Physiol.	Journal of Cellular and Comparative Physiology.
J. Cellulose Inst. Tokyo	Cellulose Industry, Journal of the Cellulose Institute, Tokyo.
J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Eng. China	Journal of Chemical Engineering, China.
J. Chem. Ind. Russ.	Journal of Chemical Industry, Russia.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Physics	Journal of Chemical Physics.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys.	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Counc. Sci. Ind. Res. Australia.	Journal of the Council of Scientific and Industrial Research of Australia.
J. Dairy Res.	Journal of Dairy Research.
J. Dairy Sci.	Journal of Dairy Science.
J. Dept. Agric. I.F.S.	Journal of the Department of Agriculture of the Irish Free State.
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture, South Australia.
J. Dept. Agric. Victoria.	Journal of the Department of Agriculture, Victoria.
J. Dept. Agric. W. Australia	Journal of the Department of Agriculture, Western Australia.
J. Ecology	Journal of Ecology.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Egypt. Med. Assoc.	Journal of the Egyptian Medical Association.
J. Electrodep. Tech. Soc.	Journal of the Electrodepositors Technical Society.
J. Exp. Biol.	Journal of Experimental Biology.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Fuel Soc. Japan	Journal of the Fuel Society of Japan.

J. Gen. Chem. Russ.	Journal of General Chemistry, Russia (formerly J. Russ. Phys. Chem. Soc.).
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Indian Chem. Soc.	Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Ind. Hyg.	Journal of Industrial Hygiene and Toxicology.
J. Infect. Dis.	Journal of Infectious Diseases.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Inst. Electr. Eng.	Journal of the Institution of Electrical Engineers.
J. Inst. Fuel.	Journal of the Institute of Fuel.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Inst. Sewage Purif.	Journal of the Institute of Sewage Purification.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Min. Agric. N. Ireland	Journal of the Ministry of Agriculture of Northern Ireland.
J. New England Water Works Assoc.	Journal of the New England Water Works Association.
J. Nutrition	Journal of Nutrition.
J. Oil Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Org. Chem.	Journal of Organic Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
J. Physical Chem.	Journal of Physical Chemistry.
J. Phys. Chem. Russ.	Shurnal Fizitscheskoi Chimii.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium	Journal de Physique et le Radium.
J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Assoc. Brit. Rubber Manufrs.	Journal of the Research Association of British Rubber Manufacturers.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Microscop. Soc.	Journal of the Royal Microscopical Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Roy. Tech. Coll.	Journal of the Royal Technical College (Glasgow).
J. Rubber Res. Inst. Malaya	Journal of the Rubber Research Institute of Malaya.
J. Sci. Hiroshima Univ.	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Sci. Tech. India	Journal of Science and Technology, India.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. South-East. Agric. Coll.	Journal of the South-Eastern Agricultural College, Wye, Kent.
J. State Med.	Journal of State Medicine.
J. Text. Inst.	Journal of the Textile Institute.
J. Univ. Bombay	Journal of the University of Bombay.

J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Kali	Kali.
Kautschuk	Kautschuk.
Keijo J. Med.	Keijo Journal of Medicine.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Agric. Exp. Stat. Bull.	Kentucky Agricultural Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloid. Shur.	Kolloidni Shurnal.
Kolloid-Z.	Kolloid-Zeitschrift.
Kunststoffe	Kunststoffe.
Lait	Le Lait.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Latvij. Univ. Raksti	Latvijas Universitātes Raksti, Kimijas Fakultātes Serija.
London Shellac Res. Bur., Tech. Paper	London Shellac Research Bureau, Technical Paper.
Louisiana Planter	Louisiana Planter.
Malay. Agric. J.	Malayan Agricultural Journal.
Mass. Agric. Exp. Sta. Bull.	Massachusetts Agricultural Experiment Station Bulletin.
Materie Plast.	Materie Plastiche.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Med. Doświad.	Medycyna Doświadczalna i Społeczna.
Mem. Accad. Lincei	Memorie della Reale Accademia Nazionale dei Lincei.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Agric. Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Inst. Chem. Ukrain. Acad. Sci.	Memoirs of the Institute of Chemistry, Ukrainian Academy of Sciences.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Mém. Soc. Ing. Civ. France	Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civils de France.
Metal Ind.	Metal Industry.
Metal Progr.	Metal Progress.
Metall u. Erz	Metall und Erz.
Metallges. Rev.	Metallgesellschaft Periodic Review.
Metallurgia	Metallurgia.
Met. & Alloys	Metals and Alloys.
Metals Tech.	Metals Technology.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Mich. Agric. Exp. Sta. Bull.	Michigan Agricultural Experiment Station Bulletin.
Mikrochem.	Mikrochemie.
Milch. Forsch.	Milchwirtschaftliches Forschungen.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Milk Ind.	Milk Industry.
Milk Plant Month.	Milk Plant Monthly.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. & Met.	Mining and Metallurgy.
Missouri Agric. Exp. Sta. Res. Bull.	Missouri Agricultural Experiment Station Research Bulletin.
Mitt. Kohlenforschungsinst. Prag	Mitteilungen des Kohlenforschungsinstituts in Prag.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Mitt. Materialprüf.	Mitteilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mitteilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Mitt. Textilforsch. Krefeld	Mitteilungen der Textilforschungsanstalt Krefeld e.V.

Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Montana Agric. Exp. Sta. Bull.	Montana Agricultural Experiment Station Bulletin.
Month. J. Inst. Metals	Monthly Journal of the Institute of Metals.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Month. Rep. Dept. Agric. N. Ireland.	Monthly Reports of the Department of Agriculture of Northern Ireland.
Mühlenlab.	Das Mühlenlaboratorium.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Butter & Cheese J.	National Butter and Cheese Journal.
Nat. Paint Var. Assoc. Circ.	National Paint, Varnish, and Lacquer Association, Inc., Circular.
Nature	Nature.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
Naturwiss.	Die Naturwissenschaften.
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletin.
New Jersey Agric. Exp. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletin.
New Phytol.	New Phytologist,
New York Agr. Expt. Sta. Bull.	New York State Agricultural Experiment Station Bulletins.
New York (Geneva) Agric. Exp. Sta. Bull.	New York (Geneva) Agricultural Experiment Station Bulletin.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nutr. Abs.	Nutrition Abstracts and Reviews.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societétens Förhandlingar, Helsingfors.
Oel u. Kohle	Oel und Kohle.
Österr. Chem.-Ztg.	Österreichische Chemiker-Zeitung.
Off. Digest	Official Digest of the Federation of Paint and Varnish Production Clubs.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletin.
Oil and Soap	Oil and Soap.
Oklahoma Agric. Exp. Sta. Bull.	Oklahoma Agricultural Experiment Station Bulletin.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Pacific Pulp and Paper Ind.	Pacific Pulp and Paper Industry.
Paint, Oil, and Chem. Rev.	Paint, Oil, and Chemical Review.
Paint Manuf.	Paint Manufacture.
Paint Tech.	Paint Technology.
Paint and Var. Prod. Man.	Paint and Varnish Production Manager.
Paper	Paper.
Paper-Maker	Paper-Maker and British Paper Trade Journal.
Paper Trade J.	Paper Trade Journal.
Papier-Fabr.	Papier-Fabrikant.
Pedology	Pedology.
Peint., Pig., Ver.	Peinture, Pigment, Vernis.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Pflüger's Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Ztg.	Pharmazeutische Zeitung.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Philippine Agric.	Philippine Agriculturist.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physics	Physics.

Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sovietunion	Physikalische Zeitschrift der Sovietunion.
Phytopath.	Phytopathology.
Phytopath. Z.	Phytopathologische Zeitschrift.
Plant Physiol.	Plant Physiology.
Plants (Z. wiss. Biol.)	Plants (Zeitschrift für wissenschaftliche Biologie).
Plast. Massi	Plastitschekie Massi.
Poultry Sci.	Poultry Science.
Proc. Acad. Sci. Agra and Oudh	Proceedings of the Academy of Sciences of the United Provinces of Agra and Oudh, India.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Amer. Gas Assocn.	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of the American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy (Tokyo).
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Internat. Cong. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. Internat. Soc. Soil Sci.	Proceedings of the International Society of Soil Science.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leningrad Dept. Inst. Fert.	Proceedings of the Leningrad Departmental Institute of Fertilisers.
Proc. Muslin Assoc.	Proceedings of the Muslim Association for the Advancement of Science.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc., Vizianagram.	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. S. Wales Inst. Eng.	Proceedings of the South Wales Institute of Engineers.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section of the Paper Makers' Association of Great Britain and Ireland.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Protoplasma	Protoplasma.
Przemysł Chem.	Przemysł Chemiczny.
Publ. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Prírodovèdeckou Facoultou Masarykovy University).
Pulp and Paper Mag. Canada	Pulp and Paper Magazine of Canada.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Queensland J. Agric.	Queensland Journal of Agriculture.
Rayon Text. Month.	Rayon Textile Monthly.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.

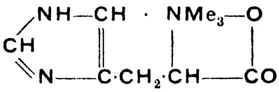
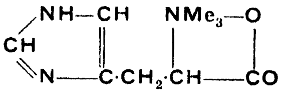
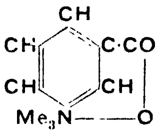
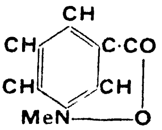
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rensselaer Polyt. Inst. Bull.	Rensselaer Polytechnic Institute Bulletin.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Res. Stud. State Coll. Washington	Research Studies of the State College of Washington.
Rev. Aluminium	Revue de l'Aluminium.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada, Órgão de Sociedade Portuguêsa de Química e Física.
Rev. Fac. Quím. Ind. Agric.	Revista de la Facultad de Química Industrial y Agrícola.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics.	Review of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sborn. Trud. Ukrain. Chim. Inst. Odessa	Sbornik Trudov Ukrainskogo Nautschno-Issledova-Telskogo Chimitscheskogo Instituta Odessa.
Science	Science.
Sci. Agric.	Scientific Agriculture.
Sci. and Cult.	Science and Culture.
Sci. et Ind.	Science et Industrie.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Mem. Univ. Saratov	Scientific Memoirs of the University of Saratov.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Quart. Nat. Univ. Peking	Science Quarterly of the National University of Peking.
Sci. Rep. Hiroshima Tech. Sch.	Scientific Reports of the Hiroshima Higher Technical School.
Sci. Rep. Tôhoku	Science Reports, Tôhoku Imperial University.
Sci. Rep. Tokyo Bunrika Daigaku	Science Reports of the Tokyo Bunrika Daigaku.
Sci. Rep. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Sect. Nat. Paint, Var. Assoc. Circ.	Scientific Section, National Paint, Varnish, and Lacquer Association, Inc., Circulars.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Scot. J. Agric.	Scottish Journal of Agriculture.
Seifens.-Ztg.	Seifensieder-Zeitung.
Sewage Works J.	Sewage Works Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collection.
Soap	Soap.
Soap Trade Rev.	Soap, Perfumery and Cosmetic Trade Review.
Soil Res.	Soil Research.
Soil Sci.	Soil Science.
Sparwirts.	Sparwirtschaft.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Stain Tech.	Stain Technology.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Steam Eng.	Steam Engineer.
Sugar Bull.	Sugar Bulletin.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Superphosphat	Superphosphat.
Superphosphate	Superphosphate.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tasmanian Agric. J.	Tasmanian Agricultural Journal.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp.
Tech. Publ. Tin Res. Counc.	Technical Publications of the International Tin Research and Development Council.

Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Teer u. Bitumen	Teer und Bitumen.
Tekn. Tidsk.	Teknisk Tidskrift.
Textilber.	Melliand Textilberichte.
Tids. Kjemi	Tidsskrift for Kjemi og Bergvesen.
Tonind.-Ztg.	Tonindustrie-Zeitung.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Amer. Soc. Mech. Eng.	Transactions of the American Society of Mechanical Engineers.
Trans. Amer. Soc. Met.	Transactions of the American Society of Metals.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Dokuchaiev Soil Inst.	Transactions of the Dokuchaiev Soil Institute.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Inst. Plast. Ind.	Transactions of the Institute of the Plastics Industry.
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry.
Trans. N. Eng. Inst. Min. Mech. Eng.	Transactions of the North of England Institute of Mining and Mechanical Engineers.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Opt. Soc.	Transactions of the Optical Society.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.
Trans. Saratov Univ.	Transactions of the Saratov University (Gelehrte Notizen der Saratover Staats Universität).
Trop. Agric.	Tropical Agriculturist (Ceylon).
Trop. Agric. (Trinidad)	Tropical Agriculture (Trinidad).
Tsch. Min. Mitt.	Mineralogische und Petrographische Mitteilungen (Zeitschrift für Kristallographie, Mineralogie, und Petrographie, Abteilung B).
U.S. Bur. Mines, Bull., Tech. Papers, and Rept. Invest.	United States Bureau of Mines, Bulletins, Technical Papers, and Reports of Investigations.
U.S. Bur. Plant Ind.	United States Bureau of Plant Industry.
U.S. Dept. Agric. Bull. (or Circ.)	United States Department of Agriculture Bulletins (or Circulars).
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
U.S. Publ. Health Rep.	United States Public Health Reports.
Ukrain. Biochem. J.	Ukrainian Biochemical Journal.
Ukrain. Chem. J.	Ukrainian Chemical Journal.
Union S. Africa Dept. Agric. Bulls.	Union of South Africa Department of Agriculture Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exp. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verfkroniek	Verfkroniek.
Verh. Geol. Reichsanst. Wien	Verhandlungen der Geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Vermont Agric. Exp. Sta. Bull.	Vermont Agricultural Experiment Station Bulletin.
Vet. Rec.	Veterinary Record.
Virginia (Blacksburg) Exp. Sta. Bull.	Virginia (Blacksburg) Experiment Station Bulletin.
Virginia Truck Exp. Sta. Bull.	Virginia Truck Experiment Station Bulletin.
Welsh J. Agric.	Welsh Journal of Agriculture.
Wiss. Veröff. Siemens-Werken	Wissenschaftliche Veröffentlichungen aus den Siemens-Werken.
Woch. Brau.	Wochenschrift für Brauerei.
World's Paper Tr. Rev.	World's Paper Trade Review.

Zavod. Lab.	Zavodskaia Laboratoriya.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Fleisch- Milch-Hyg.	Zeitschrift für Fleisch- und Milch-Hygiene.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Naturwiss.	Zeitschrift für die gesamte Naturwissenschaft.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung, Düngung, und Bodenkunde (*title now changed to* Bodenkunde und Pflanzenernährung).
Z. Pflanzenkr. Pflanzenschutz.	Zeitschrift für Pflanzenkrankheiten (Pflanzenpathologie) und Pflanzenschutz.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. pr. Geol.	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Ing.	Zeitschrift Vereins deutscher Ingenieure.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (*now changed to* Z. Wirts. Zuckerind.).
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.
Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie (Vereins der deutschen Zucker-Industrie).
Z. wiss. Biol.	Zeitschrift für wissenschaftliche Biologie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuchtung	Zeitschrift für Zuchtung.
Z. Zuckerind. Czechoslov.	Zeitschrift für die Zuckerindustrie der Čechoslovakischen Republik.
Zavod. Lab.	Zavodskaja Laboratorija.
Zellstoff u. Papier	Zellstoff und Papier.
Zement	Zement.
Zentr. Bakt.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Min.	Zentralblatt für Mineralogie, Geologie und Paläontologie.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.
Zymologica	Zymologica.

ERRATA.

(An asterisk indicates that lines are counted from the *bottom* of the page. In counting lines space occupied by chemical or mathematical formulæ, or by tabular matter, is ignored.)

Vol.	*Page*	*Line*	*For*	*Read*
I	xiv	14	AFRIDOL	AFWILLITE
I	13*a*	27	naphthaldehyde acid	naphthalic acid
I	120*b*	31*	$COOH\cdot CH_2(NH_3)_3\cdot Cl$	$COOH\cdot CH_2\cdot NMe_3Cl$
I	181*a*	33	1929, **17**, 241	1929, **77**, 241
I	199*a*	30	Curtois	Courtois
I	203*a*	4	Colin and Ricard	Ricard
I	205*c*	27	" *Celatine* "	" *Celatene* "
I	242*c*	1	" enantiomorphic "	" enantiotropic "
I	263*a*	10	**ALQUIFON**	**ALQUIFOU**
I	298*c*	33	ESPARTO	this Vol., 199*a*
I	329*b*	10*	Timmermanns	Timmermans
I	336*d*	32*, 31*	Voigtlander	Voigtlaender
I	370*a*	12	*Delete* (*v.* Chromium)	
I	468*c*	5	-arsanilite	-arsanilate
I	497*a*	12, 13	*Delete* **ARTHOFORM** (new and old) *v.* ANÆSTHETICS	
I	497*d*	30*	BALSAMS	this Vol., 616*d*
I	499*c*	7	" aminatos "	" amiantos "
I	550*a*	14	**AUSTENITE**	**AUSTRALENE**
I	550*a*	30	*Delete* **AUSTROCAMPHENE** *v.* CAMPHENE	
I	582*c*	(*below* 12)	$R\cdot N{:}N \rightleftharpoons N \rightleftharpoons R\cdot N\cdot \quad N\vdots N$	$R\cdot N{:}N< \quad N \rightleftharpoons R\cdot N\cdot \quad N\vdots N$
I	630*a*	13	thiobarbi-	thiobarbituric
I	662*d*	7*	*Delete* **BEET-ROOT GUM** *v.* GUMS.	
I	686*d*	(*above* 16*)		
I	686*d*	(*bottom*)		

A DICTIONARY OF APPLIED CHEMISTRY.

A

A-ACID. 1 : 7-Dihydroxynaphthalene-3 : 6-disulphonic acid. Intermediate product for the manufacture of dyes.

a-ACID. *Badische acid.* β-naphthylamine-[illegible]-sulphonic acid.

ABACA FIBRE. Manila hemp obtained from the leafsheath of *Musa textilis*, a variety of plantain, is quite different from hemp properly so-called, which is bast fibre from the bark of *Cannabis sativa*. The better grades are especially valuable for making ships' cables or for transmission ropes where resistance to sea-water or great strength and flexibility are required. *Musa sapientum*, the common banana or plantain, also supplies a fibre.

ABAKU NUTS *v.* Bassia Fats.

ABALAK. A formaldehyde-phenol resin used in varnishes.

ABALONE. The name given in California to various species of the edible mollusc *Haliotis*. The shell of these animals yields mother-of-pearl and is used in button-making and inlaying. For the preparation of glycogen from the abalone *H. rufescens*, *v.* L. G. Petree and C. L. Alsberg (J. Biol. Chem. 1929, **82**, 385 ; A. 1929, 838).

ABALYN. Methyl esters of abietic acid. A non-solvent ingredient in nitrocellulose lacquers. Boiling range, 360°–370°. Flash point (open), 190°, d^{20}_{20} 1·033–1·043, n^{20}_{D} 1·5297.

ABASIN. *Acetyl adalin.* Trade name for acetyl a-bromo-a-ethylbutyryl carbamide,

$$CBr(C_2H_5)_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}COCH_3$$

m.p. 109°. Used as a sedative.

ABASSI COTTON. White Egyptian cotton.

ABDERHALDEN REACTION. 1% aqueous solution of triketohydrindene (*ninhydrin*) boiled with proteins, peptones or certain amino-acids becomes bluish-violet, originally described by Ruhemann (J.C.S. 1911, **99**, 793).

The interferometric method of employing the reaction is described by J. Wadel (Fermentforsch. 1934, **14**, 266 ; A. 1934, 1138).

ABDOCAIN. *Aethocaine. Novocaine. Procaine.* Trade names for β-diethylaminoethyl-*p*-aminobenzoate hydrochloride,

$$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_2H_4N(C_2H_5)_2{\cdot}HCl$$

Used as a local anæsthetic.

ABELITE. The military type of this explosive contained ammonium nitrate 83% and trinitrotoluene 17%. Two forms, namely Abelite No. 1 and Abelite No. 4, were approved for coal mining. Abelite No. 1 contained ammonium nitrate 68·5%, trinitrotoluene 7%, dinitrobenzene 7%, and sodium chloride 17·5%, whereas Abelite No. 4 contained ammonium nitrate 67%, trinitrotoluene 14·5%, sodium chloride 7%, and starch 11·5%. H. S.

ABIES. The generic name for the Silver Firs. *A. balsamea* furnishes the oleo-resin Canada Balsam (about 66% resin and 33% volatile oil chiefly *l*-a-pinene). Its wood is used for the manufacture of cellulose (woodpulp). Strasbourg turpentine, now only of historical interest, is the exudation of *A. pectinata*. *A. Douglasii* supplies Oregon balsam. Siberian pine needle oil, oil of pine, is distilled from the leaves of *A. siberica*. It contains about 40% bornyl acetate and has been used for the manufacture of synthetic camphor. The literature of the products from Abies species, *e.g.* terpenes, resins, tannins, glucosides, abietene, abietinolic, abietolic, abietic acids, is summarised by C. Wehmer in Die Pflanzenstoffe, I, 1929 and Erganzungsband, 1935. J. N. G.

ABIETENE. The name given to the hydrocarbon produced by the dry distillation of abietic acid (Kraemer and Spilker, Ber. 1899, **32**, 2953), is also prepared by distillation of abietyl chloride at ordinary pressures (Levy, Ber. 1906, **39**, 3043). It has the formula $C_{18}H_{28}$, or $C_{19}H_{30}$. When dehydrogenated with sulphur it yields retene (Aschan, Ber. 1922, **55** [B], 2944) and on reduction with phosphorus and hydriodic acid a fluorescent hydrocarbon is produced identical with the "dodecahydroretene" of Liebermann and Spiegel (Ber. 1889, **22**, 780). It is probably decahydroretene, but no definite structure has as yet been assigned to it (Ruzicka, Helv. Chim. Acta, 1933, **16**, 169). It has b.p. 200°–202°/17 mm. or 340°–350°/760 mm., and sp.gr. about 0·99.

The hydrocarbon may be sulphonated by running into cold sulphuric acid, allowing to stand, and precipitating the product by dilution with water. The derivative finds application as a wetting agent (Gubelmann, Wieland and Henke, Ind. Eng. Chem. 1931, **23**, 1462 ; and various patents).

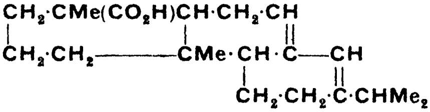
The name *abietene* is also given to a certain product obtained by fractionating the exudation of *Pinus sabiniana*, a conifer indigenous to California. It has been shown by T. E. Thorpe (Trans. Chem. Soc. 1879, **35**, 296 ; Phil. Trans. 1884, **174**, 269) to consist mainly of normal *heptane*, C_7H_{16}, mixed with a small quantity of a resin which imparts a characteristic odour.

ABIETENOL. The alcohol $C_{20}H_{32}O$, b.p. 169°–172°/0·2 mm., d_4^{17} 1·0305, n_D^{17} 1·5487, prepared by reducing the methyl or ethyl ester of abietic acid with sodium and alcohol (Ruzicka and Meyer, Helv. Chim. Acta, 1922, **5**, 581).

ABIETIC ACID. An acid derived from colophony and other resins (Dupont and Uzac, Bull. Soc. chim. 1924, **35**, 394). It may be isolated by digesting the resin with alcohol and subsequently recrystallising the crude product (Maly, Annalen, 1864, **129**, 54 ; **132**, 249 ; Ellingson, J. Amer. Chem. Soc. 1914, **36**, 325 ; Cohn, Chem.-Ztg. 1916, **40**, 791 ; Steele, J. Amer. Chem. Soc. 1922, **44**, 1933). Abietic acid may also be obtained by distilling the resin in superheated steam (Easterfield and Bagley, J.C.S. 1904, **85**, 1238 ; Johannson, Arkiv Kemi, Min., Geol. 1917, **6**, No. 19), or under reduced pressure. After recrystallisation from alcohol, in which it is fairly soluble, the melting-points observed were 150°–152° (Ellingson, *l.c.*), and 161°–165° (Steele, *l.c.*).

Abietic acid is usually present in the resin in the *dextro-* form, but may be transformed into the *lævo-* by the action of heat or mineral acid (Schulz, Chem.-Ztg. 1917, **41**, 666 ; Ruzicka and Schinz, Helv. Chim. Acta, 1923, **6**, 662). In this connection it is interesting to note that Zelinski (Ber. 1931, **64** [B], 2130) has suggested that the optically active constituents of petroleum may contain decomposition products of abietic acid.

It has been suggested by Knecht (J. Soc. Dyers and Col. 1919, **35**, 148 ; 1923, **39**, 338) that abietic acid is present in the resin as its anhydride, but this suggestion has been refuted by Schorgen (J. Amer. Chem. Soc. 1923, **45**, 1339), Ruzicka and Pfeiffer (Helv. Chim. Acta, 1925, **8**, 632) and Dupont and Uzac (Chim. et Ind. 1925, Special No. 482). Madinaveitia (Anal. Fís. Quím. 1922, **20**, 183) claims to have confirmed the molecular formula $C_{19}H_{28}O_2$ advanced by Easterfield and Bagley, J.C.S. 1904, **85**, 1238, but the greater part of the more recent evidence favours the $C_{20}H_{30}O_2$ formula as proposed by P. Levy (Ber. 1906, **39**, 3043), Koritschoner (Z. angew. Chem. 1907, **20**, 641), Fahrion (*ibid.* 1907, **20**, 356), and Vesterberg (Ber. 1907, **40**, 120), and it is now generally accepted to be a carboxylic acid of a hydrogenated derivative of *retene* (1-methyl-7-*iso*propylphenanthrene, Bardhan and Sengupta, J.C.S. 1932, 2798) which is produced when the acid is dehydrogenated with sulphur or selenium (Ruzicka and Meyer, Helv. Chim. Acta, 1922, **5**, 315, 588), palladium-charcoal catalyst (Ruzicka, *ibid.* 1933, **16**, 842), or active charcoal (Tsukamoto, J. Pharm. Soc. Japan, 1928, **48**, 1169). Levy has shown the presence of a *cyclo*hexane ring and an *iso*propyl group (Z. anorg. Chem. 1913, **81**, 145) and Johannson (*l.c.*) has confirmed the presence of two double bonds by catalytic hydrogenation in ether solution in the presence of platinum black. This experiment has also revealed a marked difference in the activity of the two double bonds (Schaeffer, Ind. Eng. Chem., Anal. Ed. 1930, **2**, 115). The hydrocarbon abietene is produced by dry distillation of the acid (Easterfield and Bagley, *l.c.*, Kraemer and Spilker, Ber. 1899, **32**, 3614) or when the acid is distilled in steam over such catalysts as charcoal or oxides of vanadium, chromium, zinc, manganese, etc., at 350°–360° (U.S.P. 1926676). Treatment of the acid with 5% zinc chloride gave an 80% yield of octahydroretene (Rouin, Bull. Inst. Pin, 1929, 251). Ruzicka (Helv. Chim. Acta, 1932, **15**, 1285) has shown that abietic acid undergoes the Diels-Alder reaction to yield a compound with one double bond, thus suggesting that the double bonds in the parent substance are conjugated. Further proof of this fact is advanced by Arbusov (J. Gen. Chem. Russ. 1932, **2**, 806). Ruzicka has also shown the methyl groups to be in the *meta* positions (Helv. Chim. Acta, 1933, **16**, 842) and that the carboxyl group must be in the 1-position (*ibid.* p. 169). In view of all these facts the most likely formula appears to be that advanced by Ruzicka (*l.c.*) and by Vocke (Annalen, 1932, **497**, 247), viz. :



$$\begin{array}{lllll}
CH_2\cdot CMe(CO_2H) & CH\cdot CH_2\cdot & CH & & \\
| & | & \| & & \\
CH_2\cdot CH_2 \text{———} & CMe\cdot CH\cdot & C & \text{——} & CH \\
 & \quad\;\; | & & & \| \\
 & \quad CH_2\cdot CH_2\cdot & & & C\cdot CHMe_2
\end{array}$$

a formula which is supported by the more recent work of Haworth (J.C.S. 1932, 2717) and Heilbron (Pharm. J. 1934, **132**, 31).

Salts.—*Sodium abietate* has been prepared by careful neutralisation (Ellingson, J. Amer. Chem. Soc. 1913, **36**, 325) and from it the heavy metal salts are obtained which are insoluble in water but soluble in organic solvents. The *chromium, manganese, nickel, iron, cobalt, strontium, aluminium,* and *copper* salts have been described (*idem, ibid.*). The *ammonium* salt is obtained by dissolving abietic acid in dilute ammonia, but the product resinifies if concentrated ammonia is used (Cohn, Chem.-Ztg. 1916, **40**, 791). It appears that most of the crystalline salts contain excess abietic acid. Dupont and others (Bull. Soc. chim. 1926, **39**, 488) have described a crystalline sodium salt containing three molecules of abietic acid to one of sodium salt. Berger (J. pr. Chem. 1932 [ii], **133**, 331) has investigated the reactions of a solution of the sodium salt when heated. The *lead* salt has been examined by Wolff and Rabinovicz (Fettchem. Umschau, 1934, **41**, 66). Salts with amines are described by Dupont and others (*l.c.*) (A. 1929, 1040), by Balaš and Hazuková, and by Palkin and Harris (J. Amer. Chem. Soc. 1934, **56**, 1935).

Esters.—The *ethyl* ester produced by direct esterification in the presence of sulphuric acid has b.p. 176°–178°/0·5 mm., f.p. −45°, and d_{20}^{20} 1·02. The methyl ester on reduction yields abietenol (*q.v.*) which is converted by the action of PCl_5 into methyl-abietene $C_{20}H_{30}$ (Ruzicka and Meyer, Helv. Chim. Acta, 1922, **5**, 581). The esters are also formed by interaction of sodium abietate with alkyl halide or sulphate or alkylene dihalide (Kesler, J. Amer. Chem. Soc. 1927, **49**, 2898). *Vinyl abietate*, b.p. 200°–225°/6 mm. (G.P. 589970), and *cetyl abietate*, m.p. 40° (Kaufmann and Friedebach, Ber. 1922, **55** [B], 1508) have also been prepared. The ethyl ester and a hydrogenated derivative of the methyl ester have been suggested for use as solvents for nitro-cellulose lacquers (U.S.P. 1944241 ; Johnston, Ind. Eng. Chem. 1929, **21**, 688). The commercially important *glyceryl* ester, " Ester gum," is used in varnishes.

Derivatives.—The acid may be reduced catalytically to a hydroabietic acid, m.p. 176°–179°, the product being identical with that obtained by Maly using sodium and alcohol as the reducing agent. (*See also* Levy, Ber. 1926, **59** [B], 1302). Abietic acid readily reacts with atmospheric oxygen, and Dupont and Levy (Compt. rend. 1929, **189**, 763 ; 1930, **190**, 1302) have studied the process in detail and have shown that a dihydroxy-compound is the final product. The monoxy-compound has also been obtained (Shaw and Sebrell, Ind. Eng. Chem. 1926, **19**, 612). Oxidation with permanganate solution yields a mixture of several hydroxy-acids (Rau and Simonsen, J. Indian Inst. Sci. 1926, **9A**, 101 ; Levy, Ber. 1928, **61** [B], 616). Addition compounds are also readily formed with halogen hydracids in acetic acid solution (Rau and Simonsen, Indian Forest Records, 1925, **11**, 207 ; Levy, Ber. 1931, **64** [B], 2441).

Abietic acid yields on sulphonation a mixture of *sulphonic acids* which may be isolated through the barium salts. Treatment with fuming nitric acid gives a *dinitro* derivative which separates from acetone in needles, m.p. 178°–184°, $[\alpha]_D^{20}$ +44·26°. The esters of this dinitro-acid have also been prepared (Johannson, Archiv Kemi, Min., Geol. 1917, **6**, No. 19). Aschan (Ber. 1922, **55** [B], 2944) has described the derivatives produced by action of nitrosyl chloride and nitrogen trioxide.

Dubourg (Bull. Inst. Pin, 1927, No. **41**, 246) has shown that nitration of abietic acid in alcoholic solution yields decahydrodinitroretene carboxylic acid (*see also* Goldblatt, J. Amer. Chem. Soc. 1930, **52**, 2132).

Detection, Estimation, and Analysis.—Abietic acid may be detected by any of the following reactions : (1) A particle of resin is dissolved in 3–4 c.c. of 95% alcohol and 10 drops of 1% alcoholic solution of furfural added, 2 c.c. conc. sulphuric acid are allowed to run down the side of the tube and in the presence of abietic acid a red colour, changing to violet blue, is formed at the junction of the liquids (Griffon, J. Pharm. Chim. 1931, **14**, 337). (2) A solution of ferric chloride in concentrated hydrochloric acid gives a violet coloration. (3) When abietic acid is heated with dry chloroform, acetic anhydride and sulphuric acid a purple-red colour is produced, changing through violet and blue to greenish-black (Mach, Monatsh. 1893, **15**, 186).

Several methods for the estimation of abietic acid in resins have been elaborated in recent years, though the older one of Rebs (Chem. Zentr. 1907, i, 997) is still valuable. According to this method, 10 g. of the resin are heated under reflux on the water bath with 20–25 c.c. of 10% alcoholic potassium hydroxide solution for 15 minutes, the resulting soap is decomposed with dilute hydrochloric acid, the separated resin filtered off, washed with cold water, and dried. It is then powdered and extracted with 50 c.c. of hot petroleum ether and from this solution, abietic acid is precipitated by ammonia, filtered, dried on the water bath, and the ammonia driven off by gentle heating. The residue represents the amount of abietic acid in the sample. Schulz and Landa (Bull. Soc. chim. 1922 [iv], **31**, 1353) suggest a method based on the reducing action of abietic acid on mercuric acetate in acetic acid solution. The precipitated mercurous acetate is then re-dissolved, oxidised, and estimated by the chloride method of Votoček (*ibid.* 1923 [iv], **33**, 110). Gluckmann and Riasantzev (Chim. et Ind. 1933, **30**, 1290) have described a method of electrometric titration in 95% alcohol or other solvents.

For determining the foreign material present in resin, the sample is extracted with toluene in which the impurities are insoluble. Georgi (Ind. Eng. Chem., Anal. Ed. 1930, **2**, 331) has suggested a photomicrographic method for the same purpose.

Uses.—Abietic acid is used in the fermentation industry, since it can be employed both to further the action of some specific ferments as well as to inhibit the action of others. It is the " rosin " used in the paper industry for sizing purposes (Ostwald and Lorenz, Kolloid-Z. 1923, **32**, 119, 195 ; **33**, 15 ; Kanamura and Tsuchida, J. Soc. Chem. Ind. Japan, 1933, **36**, 102).

For useful reviews of the chemistry of abietic acid, *see* Bunbury, Chem. Age, 1923, **9**, 650, 678 ; Samtleben, Farben-Ztg. 1925, **30**, 2863 ; Rouin, Bull. Inst. Pin, 1929, 124.

(*See also* COLOPHONY.)

ABISOL. Trade name for a 40% solution of sodium bisulphite used as a disinfectant and preservative.

ABRACOL. Trade names *Abracol* 203, *p*-toluenesulphanilide, *Abracol* 789, *p*-toluenesulphonamide. Plasticers for lacquers.

ABRASIT. Trade name for an abrasive consisting of alumina which has been fused in an electric furnace.

ABRASIVES. The various hard substances, chiefly of mineral origin, used for abrasive purposes fall naturally into the following groups, in which the hardness is roughly inversely proportional to the complexity of chemical composition.

Element.—Diamond (*q.v.*) is the hardest of all substances (hardness = 10 on Mohs' scale). Inferior material of no use for gems is known as bort (or boart), and is crushed to powder and much used by lapidaries. Diamond powder is the only material with which diamond itself can be ground and polished. Embedded in the edge of a thin disc of soft iron, diamond powder is largely used for cutting gem-stones and thin sections of rock specimens, and also for slicing larger blocks of the harder ornamental stones. A black, compact variety of diamond known as carbonado (" carbonate " or " carbon ") is embedded in the steel crowns of rock-drills.

Amongst artificial products, steel and some other hard metals are used for abrasive purposes. The so-called crushed steel, made by quenching white-hot crucible steel, is used in the stone-cutting trade. Tantalum is an extremely hard metal and finds some applications depending on hardness.

Carbides.—Carborundum[1] (*q.v.*) or silicon carbide, **CSi** (H.=9½), is prepared artificially in the electric furnace from petroleum-coke and the purest quartz-sand, and is produced in large quantities at Niagara Falls. It is largely made into sharpening stones and grinding wheels; and sold under a variety of trade-names, *e.g.* crystolon, exolon, samite, etc. In lapidaries' work it has to a great extent taken the place of corundum; but although harder than corundum it has the disadvantage of being more brittle, and it soon rubs to flour. Boron carbide, CB_6, and boron silicide, SiB_3, are also remarkable on account of their intense hardness (H. Moissan, Compt. rend. 1894, **118**, 556)—*v.* BORON.

Some of these carbides are now produced commercially in the electric furnace at Niagara Falls, and for these products the following extension of Mohs' scale of hardness has been suggested: 11, tantalum carbide and fused zirconia; 12, tungsten carbide and fused alumina (corundum); 13, silicon carbide; 14, boron carbide; 15, diamond. R. R. Ridgway, A. H. Ballard, and B. L. Bailey (Trans. Amer. Electrochem. Soc. 1933, **63**, 369).

Oxides.—Corundum (*q.v.*), Al_2O_3 is, next to diamond, the hardest of minerals (H.=9). The impure variety, emery (*q.v.*), is not quite so hard. The crushed and graded material is made into corundum wheels and emery paper, and is much used in lapidaries' work. Artificial corundum, known by the trade names of alundum, aloxite, adamite, borocarbone, etc., is now manufactured in considerable amounts at Niagara Falls, by fusing bauxite in an electric furnace. Corubin is also an artificial corundum, formed as a by-product in the Goldschmidt thermite process.

Quartz (*q.v.*), SiO_2 (H.=7), and its several varieties find extensive applications. Millstones and grindstones are made of quartz-rock, quartzite, burrstone (or buhrstone), grit, or sandstone (*q.v.*); while scythe-stones, oilstones, and whetstones (*q.v.*) consist of hornstone, lydian-stone, and other compact varieties of quartz. In the form of sand, quartz is used as a sand-blast, in scouring-soap, for cutting and grinding marble, making sand-paper, etc. Tripoli or infusorial earth is a powdery variety of opal (hydrated silica), and is used for polishing.

Silicates.—Garnet (*q.v.*) (H.=6½–7½) is used for making emery paper and cloth; and felspar (*q.v.*) (H.=6) is also used to a small degree. Silicate rocks are employed to a small extent; *e.g.* pumice for polishing, and the millstone lava (leucite-nepheline-tephrite) of Niedermendig on the Rhine for millstones. Powdered glass (**Na-Ca** silicates) is much used as glass-paper ("sand" paper).

References.—Abrasives, Imperial Institute (Mineral Industry), London, 1929; V. L. Eardley-Wilmot, Abrasives, Canada, Dept. Mines, 1927, nos. 673, 675, 677; 1929, no. 699; H. Ries, Economic Geology, 6th edit., New York, 1930; K. Becker, Hochschmelzende Hartstoffe, Berlin, 1935. L. J. S.

ABRASTOL. *Asaprol.* Trade names for calcium 2-naphthol-1-monosulphonate,

$$[C_{10}H_6(OH)SO_3]_2Ca.$$

Powder soluble in water, has been used as an antipyretic and for preserving wines.

ABRIN *v.* ABRUS PRECATORIUS.

ABRODIL. Trade name for a 20% aqueous solution of sodium monoiodomethanesulphonate, $CH_2I{\cdot}SO_3Na$, which contains 52% of iodine. Injections are used for X-ray diagnosis (*Skiagraphy*).

ABROMA AUGUSTA. Perennial Indian Hemp or Devil's Cotton. The plant yields a strong white bast fibre, said to be superior to jute. It is used for cordage. The sap is an Indian drug.

ABROTINE, $C_{21}H_{22}ON_2$. A quinine-like alkaloid isolated by Giacosa (Jahresber. 1883, [ii], **14**, 1356) from *Artemisia abrotanum.* It is a white crystalline powder with a characteristic odour. Slightly soluble in hot water, the solution showing blue fluorescence. The *chloroplatinate,* $B{\cdot}H_2PtCl_6$, and the *sulphate,* $B_2{\cdot}H_2SO_4,6H_2O$, are described. No recent work has been done on this base.

ABRUS PRECATORIUS. Linn. (Fam. *Leguminosæ*). "Crab's eye," "Prayer Beads," "Jequirity": the so-called Indian Liquorice, also known by the following names: ratí, guanchí, gunlhá, guri-ginjá, etc. A shrub found throughout the plains of India and Burma, and on the Himalaya and other hills up to the altitude of 3,000 feet, and in Africa and the E. and W. Indies. The scarlet seeds are used by Indian goldsmiths as weights; they average 1·75 grains. They are poisonous and have been put to criminal use. The roots are sold as an indifferent substitute for liquorice. I. N. Ghatak and R. Kaup (J. Indian Chem. Soc. 1932, **9**, 383; A. 1933, 104) extracted the kernels with light petroleum and examined the fatty oil obtained. Further extraction with alcohol gave *abrine,* $C_{12}H_{14}O_2N_2$, m.p. 295°, and amorphous *abralin,* $C_{13}H_{14}O_7$, m.p. 105°. For the salts of *abrine see* Ghatak (Bull. Acad. Sci. U.P. 1934, **3**, 295; A. 1934, 1235). The same author has studied the colouring matter of the seed coat, an anthocyanin, *abranin,* a glucoside (Bull. Acad. Sci. Agra and Oudh. 1933, **3**, 69; A. 1934, 873). The characteristic toxic constituent of the seeds, *abrin,* is to be distinguished from *abrine* above mentioned. *Abrin* is a mixture of two proteins, a paraglobulin and a phytalbumose. The (injected) lethal dose of *abrin* for rabbits is 0·0016 mg. per kilo (Morgenroth and Ascher, Zentr. Bakt. 1911, **59**, 510). The red corpuscles of a dog are agglutinated by *abrin* at a dilution of 1 : 16,000,000 (L. van Itallie and W. G. Bijlsma, Toxicologie, **2**, 553, D. B. Centem, Amsterdam, 1930). Among other constituents, the seeds contain much urease (M. Wagenaar, Pharm. Weekblad, 1924, **61**, 805). For a general description of Abrus, *see* G. Watt, Commercial Products of India, 1908, **1**. J. N. G.

ABSINTH. (Absinthe, Fr.; Wermuth-extract, Ger.) A well-known liqueur which enjoys great popularity in France, the chief places of manufacture being Lyons, Montpellier, and

---

[1] So named by E. G. Acheson, in 1893, from carbon and corundum, because, before it had been analysed, it was thought to be a compound of carbon and alumina.

Pontarlier. At one time it was made in large quantities at Neufchatel in Switzerland but its manufacture and sale are now prohibited in that country. It is a spirituous liquor the chief flavouring ingredient of which is oil of wormwood or absinth (*Artemisia absinthium*), but other essential oils, such as angelica, anise, cinnamon, cloves, fennel, hyssop, and peppermint are also used in small quantities.

The process of manufacture may be divided into three stages : maceration, distillation, and coloration. In the first stage the leaves and flower tops of *artemisia absinthium* and any other flavouring ingredients which are to be used are digested with spirit. The conditions and strength of the spirit vary in accordance with the requirements and taste of the manufacturer. The usual French method is to digest, for not less than twelve hours, at a moderately high temperature, with spirit of about 85% alcoholic strength. The period may, however, be extended to several days, the strength of the spirit being reduced to about 50% and a normal temperature maintained. On the completion of the period of digestion the product is distilled and the distillate transferred to the colouring vessel.

The process of colouring varies. The original method, which is still extensively practised, is to seal the distillate hermetically in a vessel with absinth and other leaves which have been dried and finely divided. The vessel is then gently heated to a temperature of about 60°C. After cooling, the liquor is strained through a hair sieve. A more rapid method is to add directly to the distillate an infusion of fresh vegetable matter such as nettles, parsley, or spinach. By either method a green colour due to the presence of chlorophyll is imparted to the spirituous liquor. During the subsequent period of storage the liquor assumes a yellow tint, which is accepted by connoisseurs as evidence of age and high quality. Inferior varieties are prepared from grain or potato spirit to which is added various essences to give the appropriate flavour, whilst a colour approximating to that of the genuine product is obtained by the addition of chlorophyll, turmeric, and other vegetable substances. Absinth is usually diluted with water before consumption; the oils and resinous bodies derived from the plants and seeds used in manufacture are thus thrown out of solution and produce a characteristic opalescence, which in a fictitious product is obtained by the addition of gum benzoin or resinous substances.

The genuine character of reputed absinth may be fairly clearly established by the determination of the essential oils, resins, and colouring matters (Hubert, Ann. Chim. Analyt. 1901, **6**, 409, and Nivière and Hubert, Mon. Sci. 1895, 566). According to Hubert absinth has a sp.gr. of 0·8966–0·9982 and the alcoholic strength varies from 47 to 72% by volume of absolute alcohol. Samples taken from importations into the United Kingdom, before prohibition was imposed, varied in alcoholic content from about 60 to 70% whilst in the United States a range of 40–60% is legally recognised.

Although genuine absinth, taken in moderation, may be accepted as having certain valuable qualities as a cordial, it has a very injurious effect upon the nervous system of those habitually addicted to its immoderate consumption, as its characteristic bitter principle (absinthin (*q.v.*)) is physiologically harmful. The toxicity of absinth as compared with certain alcohols and other alcoholic beverages is well demonstrated in work by F. Cafferata by injection into the jugular vein of the rabbit. The respective coefficients expressed in ml. per kg. of body weight are as follows : absinth 7, amyl alcohol 0·56, ethyl alcohol 10, methyl alcohol 20, whisky 10, cognac 13 to 18, gin 18 to 20, anisette 18·5 to 20, peppermint 20 to 23, kümmel 24·5, wines 65 to 80, beers 152 to 200 (V. Ducceschi, Pavia. Arch. Ital. Biol. 1920, **70**, 93). Because of its high toxicity the sale of absinth has been legally restricted or controlled in various European countries, and even in France the proportion of oil of wormwood or other oil of similar toxic nature may not exceed 1 g. per litre. F. G. H. T.

ABSINTH, ESSENTIAL OIL OF (Oil of Wormwood). The oil distilled from the herb *Artemisia absinthium*, Linn. N.O. *Compositæ*. The herb is indigenous to many European countries and has been introduced into N. America which is now the source of the ordinary oil of commerce. The yield from the fresh herb is 0·12–0·24%.

The characters of the American oil are : d^{25} 0·917–0·942, n_D^{20} 1·460–1·474. Soluble in 3 vols. 80% alcohol.

It contains thujyl alcohol; thujone; phellandrene; pinene; thujyl acetate, *iso*valerate and palmitate; cadinene and a blue sesquiterpene possibly identical with azulene (*q.v.*).

This oil is used in the preparation of liqueurs. C. T. B.

ABSINTHIN or ABSINTHIIN, $C_{15}H_{20}O_4$. The toxic effect of absinth (*q.v.*) is due to the presence of a bitter substance, the chief flavouring, extracted with the oil from the dried leaves of wormwood (*Artemisia absinthium*). Various formulæ have been assigned to this substance, the differences being due to the difficulty of obtaining it in a pure state. It was first isolated in crystalline form by Duquesnel (Bul. gen. de Therapeutic, 1884, **107**, 438). Senger (Arch. Pharm. 1892, **230**, 103) failed to attain sufficient purity to give a crystalline product, the substance he obtained being in an amorphous form which melted at 65°. He was able, however, to establish the empirical formula $C_{15}H_{20}O_4$. This was confirmed by Bourcet (Bull. Soc. chim. 1898 [iii], **19**, 537) as applicable to his product, which was in the form of fine white prismatic crystals melting at 68°.

According to the last two workers absinthin is an unstable glycoside, readily decomposed by the action of dilute acids or even boiling water, and yielding dextrose, a volatile oil and a solid resinous body of the aromatic series. It is readily soluble in alcohol, ether, chloroform or benzene; it gives a precipitate with tannic acid and one with gold chloride which is reduced on warming. On oxidation with nitric acid it yields volatile fatty acids, whilst with potassium chromate and sulphuric acid it yields oxalic and picric acids. With Fröhde's reagent it gives a brown colour, changing first to blue and then to violet. With sulphuric acid it yields a brown colour which turns to green and then blue.

Tokohu (J. Exp. Med. 1924, **5**, 29–46), experimenting with rabbits, found that absinthin, in small quantities, promotes the absorption of grape sugar and inhibits the absorption of other substances. In larger quantities it appears to promote the absorption of amino acids.

F. G. H. T.

ABSINTHOL, *Thujone, Tanacetone,* $C_{10}H_{16}O$, is the essential principle of oil of wormwood, derived by distillation from *Artemisia absinthium*, a plant which is indigenous to most European countries, where the oil has been produced for at least four centuries. In comparatively recent times the plant has been introduced into the United States of America, whence increasing supplies of the cheaper qualities of the oil are now obtained. The chemical composition of the oil was first systematically investigated by Leblanc (Compt. rend. 1845, **21**, 379), who showed that its principal constituent has the formula $C_{10}H_{16}O$ and boils at 203°. This was confirmed by Gladstone and others (Chem. Soc. Trans. 1864, **17**, 1), and by Beilstein and Kupffer (Annalen, 1873, **170**, 290) who named it "absinthol" and identified its dehydration product with cymene. Semmler (Ber. 1892, **25**, 3350) proved absinthol to be a ketone, identical with thujone or tanacetone, which occurs largely in other essential oils such as oil of tansy, sage, and *Artemesia barelieri*.

Absinthol is a colourless oily liquid of pleasant odour, strongly dextrorotatory (about +68°), b.p. 203°, d_{20} 0·9126, $[n]_D$ 1·4495. Though isomeric with camphor it differs from that body in combining with sodium bisulphite and in not being converted into camphoric acid by means of nitric acid nor into camphocarboxylic acid by treatment with carbon dioxide and sodium.

The methods suggested by Cuniasse (J. Pharm. Chim. 1907, **25**, 180–2) and Enz (Chem. Zentr. 1911, ii, 576) for the identification of absinthol based on the presence of thujone cannot be accepted as conclusive as thujone occurs in other plants. The tests, therefore, are of negative value only, as proving the absence of oil of wormwood.

F. G. H. T.

ABSORBITE. Trade name for an activated carbon made from coconut shells and used for adsorbing gases.

ABSORPTION. When a gas or vapour is in contact with a liquid any soluble constituent of the gas distributes itself so that part or all goes into the liquid phase.

This process of *absorption* is to be distinguished from the corresponding distribution between solid and gas which is known as *adsorption* (*q.v.*).

At equilibrium a definite relation exists between the concentrations of the constituent in the gas and liquid phases. The ratio of these concentrations is known as the partition factor and is denoted by k, so that if c_g and c_l represent the concentrations in the gas and liquid phase respectively, measured in parts by weight per unit volume, then $k = c_l/c_g$.

The value of the partition factor depends on the nature of the absorbent and of the absorbable constituent and on any mutual action between the constituent and other constituents in the liquid and gas phases; it varies with temperature and sometimes with concentration.

When the gas simply dissolves in the liquid and the absorption is not complicated by chemical action, by dissociation or by association, the partition of the solute between the phases follows Henry's Law which in its simplest form states that at a fixed temperature the partition factor is a constant unaffected by concentration or pressure. If chemical combination with the solvent takes place the law does not always apply.

The effect of temperature is in general to diminish the solubility of a gas. When the solute is the vapour of a liquid miscible with the solvent the partial pressure of the vapour in the gas is equal to the vapour pressure of the pure liquid solute multiplied by its molar fraction in the solution. This may be regarded as an extension of Raoult's Law which applied originally to the solvent only.

The process of absorption is used technically either to recover a valuable constituent or to eliminate an impurity from a mixture of gases. In plant for this purpose gas and liquid remain in contact for a limited time and equilibrium between the phases is not reached. The nearness of approach to equilibrium is conditioned by the time and surface available and by the rate at which absorption takes place. A knowledge of the factors that influence this rate is necessary for the understanding of technical absorption processes.

Some of the simple essentials of the problem were considered by Hurter in 1885 and succeeding years (J.S.C.I. 1885, **4**, 639; 1887, **6**, 707; 1893, **12**, 227, 989), but a clear insight into the nature of the process was not obtained until Lewis (Ind. Eng. Chem. 1916, **8**, 825) showed that absorption is a diffusional process through non-convecting films of gas and liquid. This "film theory" as further developed by Whitman and Keats (Ind. Eng. Chem. 1922, **14**, 185; Chem. and Met. Eng. 1923, **29**, 146) postulates that the interchange of solute between two fluid phases in contact and in relative motion is instantaneous at the interface so that there is equilibrium between the phases at the surface of contact; mixture by convection is very rapid in the main body of each phase, but between the main body of either phase and the interface there is a film of the fluid any motion in which is almost entirely parallel to the interface. Movement of the solute across this film can take place only by diffusion, the rate of diffusion being proportional to the gradient of concentration across the film. It follows that for a given concentration difference across the film the rate of diffusion depends on the thickness of the film and on the specific diffusivity.

More recent investigators have shown that the assumptions made are not fully justified and that a complete statement is considerably more complicated; the two-film theory nevertheless forms the most convenient basis for the interpretation of experimental data and the application of these to industrial plant.

The factors affecting transfer across the films are combined into film transfer coefficients, k_g for the gas film and k_l for the liquid film, the weight of solute W transferred in unit time across unit area of interface being represented by $k_g \Delta C$ and $k_l \Delta c$, ΔC and Δc being the concentration differences between the two sides of the gas and liquid films respectively. When Henry's Law applies these can be combined into an overall transfer coefficient K_g so that

$$W = k_g \Delta C = k_l \Delta c = K_g(C_g - C_l)$$

where C_g is the concentration in the main body of the gas and C_l is that concentration in gas that would be in equilibrium with the main body of liquid. These three coefficients are connected by the relation

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k \cdot k_l}$$

where k is the partition factor at the interface. When k is very high the second term becomes very small in comparison with the first and when k is small the first term becomes negligibly small ; in other words, for very soluble gases the resistance of the gas film is the governing factor in the rate of absorption and when the solubility is very low the liquid film alone is of importance, *e.g.* in the absorption of ammonia by water the gas film may provide 95% of the resistance, whereas in the absorption of hydrogen sulphide the resistance of the liquid film is more than 98% of the whole. For such absorptions as that of benzene vapour by gas oil or of sulphur dioxide by water, the two resistances are of the same order (Hollings and Silver, Trans. Inst. Chem. Eng. 1934, **12**, 49).

Much work has been done in evaluating the effect of various factors on the gas film coefficient ; for example Gilliland and Sherwood (Ind. Eng. Chem. 1934, **26**, 516) have combined the effects of diffusivity, density, viscosity, pressure and gas velocity into a single expression applying to absorption in cylindrical tubes. Much less is known concerning the liquid film coefficient ; this however is of less importance industrially, for where possible an absorbent is usually chosen in which the solubility of the constituent to be removed is high.

In order that high rates of absorption may be obtained in practice attention must be directed to the provision of large areas of contact between liquid and gas and to the maintenance of high rates of transfer across these surfaces. The large contact surfaces necessary are obtained in one of three ways : (*a*) bubbling the gas through the liquid, (*b*) spraying the liquid through the path of the gas and (*c*) passing the gas over surfaces wetted with the liquid. All these methods are used in practice. Bubbling gives very high rates of transfer if the bubbles are small as the liquid film tends to be stripped off by the upward passage of the bubble and the distance for gaseous diffusion is also small. Large contact surface is provided, but the pressure necessary to overcome the hydraulic head is high and countercurrent working is difficult to arrange. Spraying also provides large surfaces but there is considerable tendency for the smaller droplets to be carried forward with the gas stream. By the use of wetted surfaces very large velocities can be employed without high back pressure and with very little risk of entrainment of liquid. Thin films of liquid can be used and high rates of absorption may be obtained for all types of solutes.

In practice it is usually desirable to use as small a quantity of absorbent as possible to remove the maximum proportion of soluble constituent. It becomes necessary therefore to employ the countercurrent principle so that the gas leaving the apparatus has been in contact with the least concentrated solution, whilst the liquid leaves after final contact with the concentrated entering gas. It can be shown that the minimum quantity q of liquid required to remove all the solute from unit volume of the gas in a countercurrent washer is given by

$$qk = 1$$

where k is the partition factor. This assumes that equilibrium is reached in all parts of the apparatus. In practice this quantity of liquid has to be somewhat increased to allow for the imperfections of working and for the fact that equilibrium is not attained.

When the quantity of absorbent required is very small it becomes very difficult to distribute it evenly over the cross-section of a countercurrent absorption plant or washer of sufficient diameter to pass the volume of gas ; the volume of liquid may even be insufficient to wet the whole of the washing surfaces or to provide a continuous and pervading spray. In these circumstances it becomes necessary to depart somewhat from true countercurrent flow and to divide the apparatus into a number of stages, in each of which the liquid is recirculated at high rates, while at the same time liquid introduced into one end of the plant gravitates from stage to stage in countercurrent to the general flow of the gas. Such pieces of plant are known as multi-stage washers.

When the absorption is one where the gas has no tendency to leave the liquid phase after having entered it, for example where chemical combination occurs as in the absorption of ammonia by sulphuric acid, there is no advantage to be gained from countercurrent working and a single stage apparatus is all that is required.

True countercurrent absorption plant usually takes the form of the tower scrubber, a vertical cylindrical or rectangular tower either empty or filled with some form of packing. The packing may consist of wooden boards, uniformly graded coke, flints, etc., or of specially manufactured forms such as metal or ceramic rings, spirals, helices, etc., all of which are designed to present large wetted surfaces and to subdivide the gas stream finely and evenly while offering a minimum resistance to the flow of gas. The liquid is distributed usually in the form of spray, at the top of the tower, and trickles down over the surface of the filling whilst the gas, admitted at the bottom, simultaneously makes its way upwards through the interstices. When no packing is employed the gas makes contact with a fine spray of liquid falling down the tower.

Of the forms of packing the wooden grid type is the most widely used. The grids consist generally of parallel boards on edge from ⅛–½ in. in thickness, 1–12 ins. wide, spaced from ⅜–1 in. apart. With thin boards a greater proportion of free space is obtained and the tower can be made somewhat smaller.

The grids in successive layers are arranged at right angles to one another, or have their axes at a slight angle to those below so that the whole forms a stepped helix, the object of either arrangement being to ensure the maximum baffling of the gas stream. Serrated lower edges to the boards prevent the liquid running along to one end. If the tower is a tall one a space is left between tiers at intervals of a few feet to allow redistribution of the gas.

Metal and ceramic rings of various special forms are widely used in the chemical industry. The material is chosen to resist attack by the fluids and the design is such as to present a very large surface. The first cost is, however, comparatively high.

Various devices are employed to distribute the liquid evenly over the upper surface of the packing, one very effective example consisting of a small plate or cone placed 3 ft. vertically below a jet, so that the stream of liquid breaks up into a series of drops before it strikes the plate and is then thrown outwards in a well-distributed spray.

In a practical tower-scrubber, since equilibrium between the phases is not reached, it follows that a certain part of the soluble constituent in the gas is not removed by the liquid. This proportion depends on the dimensions of the scrubber, the nature and conditions of the absorption, and on the quantities of gas and liquid passing. By making a number of simplifying assumptions the following expression has been derived for the performance of a tower-scrubber (Hollings and Silver, *ibid.*):

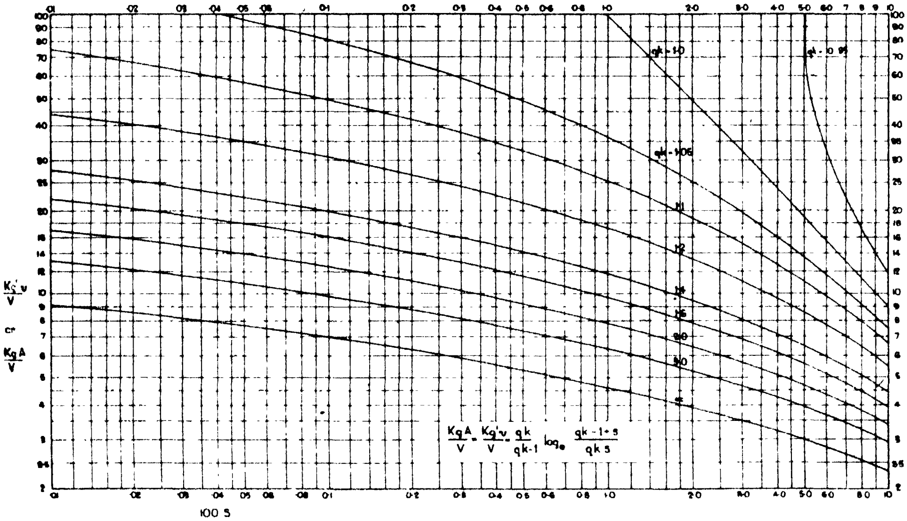


Fig. 1.

$$\frac{K_gA}{V} = \frac{qk}{qk-1}\log_e\left(\frac{qk-1+S}{qkS}\right)$$

where K_g is the overall transfer coefficient = lbs. absorbed per hour per sq. ft. of interface for a gas concentration difference of 1 lb. per cu. ft. of gas.

A is the total area of gas-liquid interface in the tower.

V is the volume in cu. ft. of gas passing per hour.

S is the proportion of soluble constituent in the gas that escapes unabsorbed. When the feed liquid already contains some of the soluble constituent, S represents the proportion unabsorbed, not of the total concentration in the gas, but of that part of the concentrates which is in excess of that in equilibrium with the feed liquid.

k is the partition factor.

q is the ratio of the volume of absorbent to the volume of gas washed.

When $qk = 1$ this expression reduces to

$$\frac{K_gA}{V} = \frac{1}{S} - 1$$

The proportion unabsorbed decreases progressively as the volume of washing liquid is increased, but there is a minimum below which this cannot be reduced, for if q be put equal to infinity the expression reduces to

$$\log_e S = -\frac{K_gA}{V}$$

The conditions in technical tower-scrubbers are usually such that the above expressions are not quite accurate, but they permit of a close approximation to the actual performance of such plant.

The use of the equation is made much easier by the graph in Fig. 1 which shows the relation between the group $\frac{K_gA}{V}$ and S for various values of qk.

Multi-Stage Washers.—The above equations are not applicable to multi-stage absorption plant, typical examples of which are briefly described below. Such washers may be classified according to which of the three methods of obtaining contact is adopted.

Bubbling type washers are not extensively used. They usually consist of a series of superposed chambers, each provided with a liquor overflow into the chamber below which maintains a constant level of liquid in the chamber. The gas passes upward from chamber to chamber, emerging in each through some device below the surface of the liquid which is designed to subdivide the gas into a large number of bubbles, usually by passage through a number of orifices or serrations. The high back pressure necessary to force the gas through the series of heads of liquid is a considerable disadvantage when washing gas at low or atmospheric pressure.

The *spraying* method of making contact is adopted in centrifugal washers, of which the original type and the most widely used is the Feld washer, which consists of a vertical cylindrical vessel divided into a number of superposed chambers by stationary troughs fitting closely around a central shaft. Attached to the shaft are concentric conical baskets dipping into the troughs. The shaft and baskets revolve at high speed, flinging the liquid across the gas space in the form of a fine evenly spread spray. The gas enters near the bottom and passes upwards through the successive layers of spray. This type of plant is used in the coking industry for the absorption of benzole by gas oil and for the extraction of ammonia by water from coke-oven gas. A considerable amount of power is required to drive the shaft, but the resistance to gas flow is very low.

Of multi-stage absorption plant using *wetted surfaces* there is a greater diversity of types. The stages are usually arranged in horizontal succession. The means adopted for recirculation of liquid in each stage consist either of dipping the surfaces bodily into the liquid as in the rotary type or pumping the liquid that has run away from the bottom of the packing back to the sprays as in the static type.

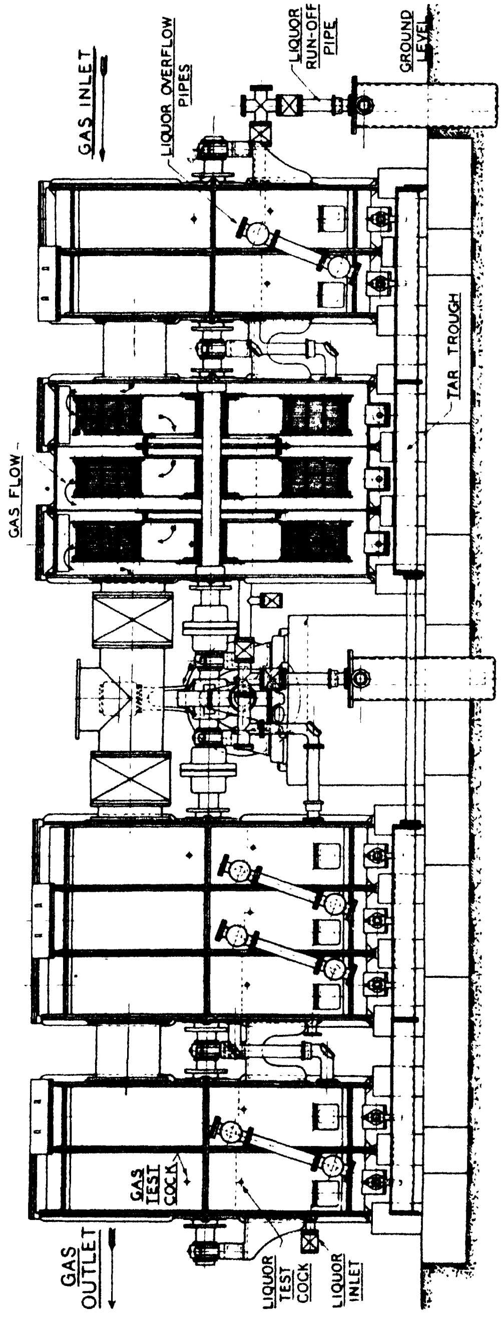


FIG. 2.

Washers of the rotary type consist of one or more co-axial cylinders which are divided, by vertical partitions provided with gasways, into a number of cylindrical chambers, the bottom of which contains the washing liquid. Along the axis is a horizontal shaft to which is attached, in each chamber or bay, the material which provides the washing surfaces. These may be either boards or metal plates or brushes. As the shaft revolves the surfaces of this filling dip into the liquid contained in the chambers. Gas passes through the series from end to end whilst the liquid enters at the end at which the gas leaves and overflows from bay to bay countercurrent to the gas. An example of this type is the Whessoe washer shown in Fig. 2 in which the filling medium takes the form of wooden boards.

The static type of washer consists of a number of chambers containing the filling built into a rectangular block. Each chamber is provided with a separate pump which circulates liquid from the bottom of the chamber back to the sprays above the packing. Liquid is fed into the end chamber and gravitates from bay to bay; the gas passes through in the opposite direction. The flow of gas and liquid within each bay may be countercurrent, concurrent, or at right angles. In the last case the gas passes horizontally through the packing down which the liquid is flowing. An example of this type is the Holmes "Multi-film" washer illustrated in Fig. 3.

In a theoretical treatment of the multi-stage washer Silver has shown (Trans. Inst. Chem. Eng. 1934, **12**, 64) that if equilibrium were reached in each bay the proportion of the initial content of soluble constituent in the gas that remains unabsorbed would be given by

$$S = \frac{qk-1}{(qk)^{n+1}-1}$$

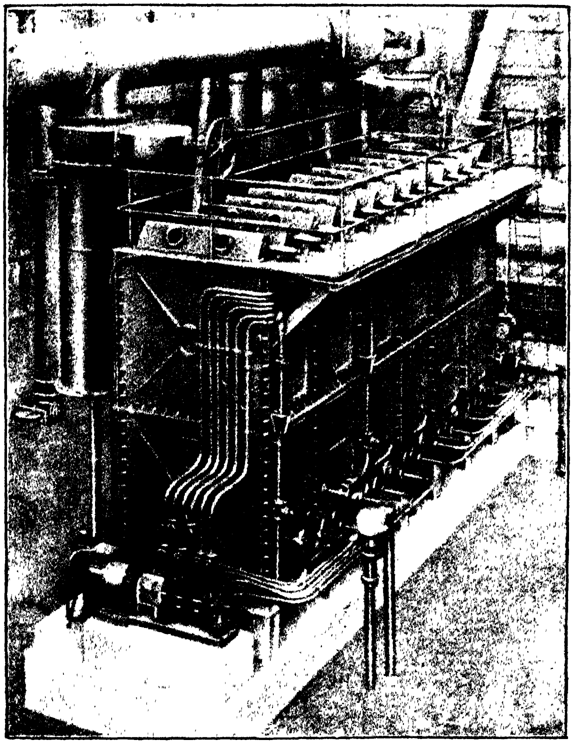


FIG. 3.

where n is the number of bays in the washer. When $qk = 1$ this becomes

$$S = \frac{1}{n+1}$$

In practice equilibrium is not reached in the bays and the proportion unabsorbed is given by

$$\log \frac{qkS}{qk-1+S} = n \log \left(\frac{E}{qk} + 1 - E\right)$$

where E represents the efficiency of absorption in each bay and is defined as the ratio of the amount absorbed in the bay to the amount that would be absorbed if the gas came to equilibrium with the liquid in the bay.

When $qk = 1$ $S = \frac{1}{nE+1}$

and when qk is very large $S = (1-E)^n$.

The efficiency E of good multi-stage washers working at their normal load is usually between 0·6 and 0·9.

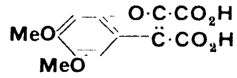
It has already been stated that multi-stage washers are more suitable than tower-scrubbers for the absorption of gases whose solubility is so high that only small quantities of washing liquid are required. They are not suitable for sparingly soluble gases, for in order to maintain high efficiencies the volumes that would require to be circulated in each bay become too large to be practicable. Fortunately the tower-scrubber deals satisfactorily with these absorptions.

As examples in which the volumes of liquid required are large enough for the successful use of tower-scrubbers the following are mentioned.

The absorption of sulphur dioxide from flue gases by calcium bicarbonate solution (Pearson, Nonhebel and Ulander, J. Inst. Fuel, 1935, **8**, 119) in which 80–140 gallons of liquid are passed over the tower per 1,000 cu. ft. of gas. The absorption of benzole vapours from coal gas in which 7–10 gallons of gas oil are circulated per 1,000 cu. ft. of gas. This is approaching the lower limit for effective distribution, but with well designed distributors and packing good results are obtained. The same operation is just within the capacity of rotary washers but the bay efficiency and the proportion recovered are rather low. Somewhat better results might be anticipated from plant of the static multi-stage type.

An operation that is carried out with great success in multi-stage washers is the absorption of ammonia from coal gas by water. The quantity of absorbent required is very small, only 0·3–1 gallon per 1,000 cu. ft. of gas, which is far too small a quantity to irrigate the packing in a tower-scrubber. H. H. and L. S.

ABUTIC ACID. One of the degradation products of the ketone rotenone obtained from derris root. According to S. Takei, S. Miyajami, and M. Ono (Ber. 1932, **65** [B], 1041 ; A. 1932, 860) its structure is



The dimethyl ester has m.p. 156°.

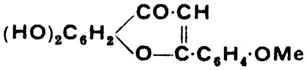
ABUTILON INDICUM. (Fam. *Malvaceæ.*) The bark of this tree and of the allied species *A. asiaticum* yields long white fibres ; much mucilage is contained in the leaves, roots, and seeds. *A. avicennæ*, the Indian mallow, supplies the fibres known as China jute.

ABYSSINIAN GOLD. A yellow alloy of copper and zinc coated with gold. The prepared slab of brass, containing 90·7% copper and 8·3% zinc, is plated on one side only with gold and is then rolled out into sheets from which articles of jewellery are formed in the usual way. It is known also as Talmi gold. The term is sometimes applied in trade to aluminium bronze.

ABYSSINIAN TEA. *Arabian tea.* The dried leaves of a small tree *Catha edulis* found in Abyssinia and S.W. Arabia. The leaves contain the three alkaloids *d*-nor*iso*ephedrine (cathine), cathidine, and cathinine. Its action is that of a stimulant narcotic.

ACACATECHIN, $C_{15}H_{14}O_6$. Crystals, m.p. 204°–205°. Was obtained from cutch, *i.e.* black catechu prepared from *Acacia catechu.* According to K. Freudenberg and L. Purrmann (Annalen, 1924, **437**, 274 ; A. 1924, **1**, 868) this substance consists largely of *dl*-catechin with some *l*-epicatechin.

ACACETIN. 5 : 7-Dihydroxy-4′-methoxyflavone,



$$(HO)_2C_6H_2<\begin{matrix}CO\cdot CH\\ \| \\ O{-}C\cdot C_6H_4\cdot OMe\end{matrix}$$

m.p. 258°–259°. Found in the leaves of *Robinia pseudacacia* (*cf.* Acaciin). Synthesised by Robinson and Venkatamaran (J.C.S. 1926, 2348) (*v.* ROBINIA PSEUDACACIA).

ACACIA BARK. *Balbul bark. Wattle bark.* Two species of Acacia, *A. arabica* or balbul of the Eastern tropics, and *A. decurrens*, Australian wattle, supply the bark which yields an astringent decoction used in medicine. Balbul contains 20% tannin and wattle 22–36%. These and other varieties of acacia bark are employed in tanning. *A. pycnantha*, golden wattle, and *A. dealbata*, silver wattle, are exported from Australia, and the pods of *A. nilotica* (or nebneb) and of other African species are also utilised.

ACACIA CATECHU. (*Black catechu ; Cutch ; Kutch.*) Cutch is the evaporated extract of the heartwood of the tree growing in Eastern India and Burma. It forms hard, brittle dark brown to black masses, containing 25–30% of catechu-tannic acid and 2–10% of acacatechin. It is administered internally as a powerful astringent. It is used in tanning and for dyeing brown shades on cotton, and as an ingredient in " boiler fluids " (*v.* CATECHU or CUTCH).

ACACIA CAVENA is grown in the South of France for the essential oil contained in its flowers.

ACACIA DEALBATA yields the mimosa perfume.

ACACIA FARNESIANA is the source of oil of cassie containing methyl salicylate, benzaldehyde and benzyl alcohol, but its valuable component is a ketone, b.p. 133°/15 mm., which has an odour of violets.

Cassie oil is to be distinguished from cassia oil from *Cinnamomum cassia.*

ACACIA GUM. This gum is the principal variety of what is commonly termed *gum arabic.* The gum in a moist condition exudes from the stem and branches of *Acacia Senegal*, a small tree indigenous to East and West Africa, and of some other species of *Acacia* (N.O. *Leguminosæ*).

The soluble gum produced in the Sudan has been known as an article of commerce since the first century. It was shipped to Arabian ports, and thence transferred to Europe, hence its name as gum arabic. The best gum is collected from the grey-backed acacia tree, known locally as " hashab." Inferior varieties are obtained from the red- and white-backed acacias, and are known locally as " talh " and " talha." A certain amount is collected in the Blue Nile district, and there is a good trade in the gum at Gedarif, which lies between the Blue Nile and Abyssinia. The province of Kordofan is the principal seat of the gum collecting industry.

The gummy exudation loses about 15% of water by evaporation and is found usually in the form of rounded or ovoid tears, or angular fragments with glistening surfaces, nearly colourless or of a yellowish tint. It is soluble in an equal amount of water forming a slightly acid mucilage which is not ropy or glairy. It is used as an adhesive, and is a good emulsifying agent.

It is official in the British Pharmacopœia, which requires that it shall not lose more than

15% on drying at 100°, and shall not contain more than 5% of ash. It does not give a blue or brown colour when a cooled boiled solution is treated with a drop of iodine solution (absence of starch and dextrin); nor a bluish-black colour with ferric chloride solution (absence of tannin).

Gum acacia is composed mainly of the calcium (with slight traces of magnesium and potassium) salt of arabin or arabic acid, which can be obtained in a fairly pure condition by acidifying an aqueous solution with **HCl**, and dialysing. Pure gum acacia does not reduce Fehling's solution, unless traces of contaminating sugars are present.

According to Butler and Cretcher (J. Amer. Chem. Soc. 1929, **51**, 1519) arabic acid is composed of one molecule of *d*-glycuronic acid, three molecules of *d*-galactose and of *l*-arabinose, and one molecule of *l*-rhamnose, these being the products of the quantitative hydrolysis of the acid.

A full account of the industry will be found in the Bulletin of the Imperial Institute (No. **63**).

The gum produced in the French colony Senegal is also mainly derived from *Acacia Senegal*, the value of the export of which is about £70,000 per annum, as against up to £225,000 per annum of Sudan gum from Egypt.

For an exhaustive spectroscopic examination of gum acacia, *see* Judd Lewis and Wombwell (Quart. J. Pharm. 1933, **6**, 475).

In medicine, acacia is used in the preparation of lozenges, as a pill excipient, and as a demulcent in cough mixtures and similar preparations.

E. J. P.

ACACIAS *v.* TANNINS.

ACACIIN, $C_{28}H_{32}O_{13}$, m.p. 260° with decomposition. A flavone glycoside from the leaves of *Robinia pseudacacia*, is hydrolysed to two molecules of rhamnose and acacetin, which is 4′-methyl-apigenin, *i.e.* 5 : 7-dihydroxy-4′-methoxy-flavone. It is deduced from the absorption spectrum that the point of attachment of the sugar is to the 7-hydroxyl group (Hattori, Acta Phytochim. 1928, **4**, 41, 63).

E. F. A.

ACAJOU. *Cashew Nuts. Anacardium Occidentale, q.v.*

ACALYPHA INDICA. The drug is a dried plant growing in Central India. It contains the alkaloid *acalyphine*, acts as an expectorant and emetic, and has been used instead of ipecacuanha.

ACANTHITE *v.* ARGENTITE.

ACAROID RESIN. *Gum Accroides. Xanthorrhœa Balsams.* The yellow variety from *X. hastilis* and the red from *X. arborea* and *X. australis* are used for spirit varnishes.

ACCELERATORS. Substances used in the rubber industry which accelerate and facilitate vulcanisation, (*a*) inorganic, some of which also produce other effects as pigments or fillers, *e.g.* antimony pentasulphide, litharge, lead thiosulphate, lime, magnesia and magnesium carbonate; (*b*) many organic nitrogen compounds of which 0·1–0·2% may be sufficient, *e.g.* hexamethylenetetramine, aniline, thiocarbanilide, di- and tri-phenylguanidine, *p*-nitrosodimethylaniline; (*c*) the dithiocarbamates, *e.g.* methyl dithiocarbamate: the thiouram disulphides; (*d*) nitrogen-free organic accelerators, *e.g.* xanthogenates of **Na**, **K**, **Zn**, and **Pb** in presence of **ZnO**. Some of these enable vulcanisation to be carried out at lower temperatures than usual with an improvement in the durability and resistance to wear of the goods.

J. N. G.

ACCEPTOR. A substance (**A**) which normally is not oxidised by oxygen (or reduced by hydrogen) but is oxidised (or reduced) when in presence of another substance termed the *inductor* (**I**) which itself is undergoing oxidation (or reduction) by a third substance the *actor* (RO_2) in accordance with the scheme (1).

$$(1)\ I+RO_2=IO+R+O. \quad A+O=AO$$
$$(2)\ I+H_2O=IO+2H. \quad A+2H=AH_2$$

(2) is an enzyme reaction, illustrating the reduction of **A**.

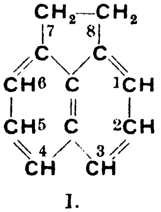
ACCRA COPAL. West African resin used for varnishes.

ACEDICONE. *Acedicoin.* Trade name for acetylcodeine, acetyldemethylo-dihydrothebaine. Analgesic. (*V.* OPIUM.)

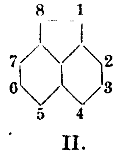
ACEDRONOLES (Badische). Trade name for primary aromatic amines and diamines used in producing insoluble azo dyes on acetylcellulose.

ACENAPHTHENE. A hydrocarbon, $C_{12}H_{10}$, occurring to a small extent in the anthracene fraction of coal tar, from which it may be isolated by careful fractionation and purified by crystallisation from alcohol (Kiprianov and Daschevski, Amer. Chem. Abstr. 1933, **27**, 5516). Crystallisation of the picrate or sublimation of the hydrocarbon in the vapours of a selective solvent (B.P. 364628, 364723) have also been suggested as methods of purification.

Acenaphthene can be synthesised by the Kishner-Wolff reduction of acenaphthenequinone disemicarbazone with sodium in absolute alcohol at 200° for 12 hours (Schönberg, Ber. 1921, **54** [B], 2838). It has the structure I,



I.



II.

and melts at 95° and boils at 278°.

Morgan and Stanley (J.S.C.I. 1925, **44**, 493T) have suggested an alternative rational method of numbering the carbon atoms, II.

Acenaphthene vapour, when passed through a quartz tube heated to redness, is partially dehydrogenated to yield *acenaphthylene*, m.p. 93°, b.p. 270°, an unsaturated hydrocarbon of similar structure, but with a double bond between the carbon atoms (7 and 8) of the bridge (Dziewoński and Rapalski, Ber. 1912, **45**, 2491; Goswami, Compt. rend. 1924, **179**, 1269). The dehydrogenation of acenaphthene is also catalysed by magnesium, aluminium, and zinc oxides and by zinc molybdate. Pure acenaphthylene may be recovered from the recrystallised picrate; it yields the dichloride, m.p. 115°, when a solution in chloroform is treated with chlorine.

When acenaphthene is hydrogenated under pressure in the presence of nickel, it yields first the tetrahydro- and then the decahydro-derivative (Ipatieff, Ber. 1909, **42**, 2092). Goswami (*l.c.*) records the boiling-points of these compounds as 240° and 235° respectively. It has also been shown that by careful regulation of the experimental conditions and the nature of the catalyst, either of the products may be obtained in a practically pure state (von Braun and Kirschbaum, Ber. 1922, **55** [B], 1080).

If acenaphthene is oxidised with sodium dichromate and sulphuric acid, a 40% yield of naphthalic acid (naphthalene-1 : 8-dicarboxylic acid) is obtained (Ullmann and Cassirer, Ber. 1910, **43**, 439). The catalytic oxidation under high pressure has been examined (Paillard and Duckert, Helv. Chim. Acta, 1933, **16**, 773) and it has also been shown that when acenaphthene vapour is passed over a vanadium pentoxide-pumice catalyst at 400° the product contains acenaphthene-quinone, naphthalic anhydride, and naphthaldehyde-acid, while Marquis (Compt. rend. 1926, **182**, 1227) finds that careful oxidation with lead peroxide in acetic acid gives a 30% yield of acenaphthenol, m.p. 148°.

Amongst the molecular addition compounds, suitable for purposes of identification, are the *picrate*, m.p. 161° ; the *styphnate*, m.p. 156° (Efremov, J. Russ. Phys. Chem. Soc. 1918, **50**, I, 372 ; **51**, 353) ; and the *m-dinitrobenzene* compound, m.p. 73·5° (Karvé and Sudborough, J. Indian Inst. Sci. 1921, **4**, 159).

DERIVATIVES.

Nitro-derivatives.—The 4-*nitro* compound may be obtained by reaction between equivalent quantities of acenaphthene and acetyl nitrate (Ferrario and Weber, Arch. Sci. phys. nat. 1908, **25**, 517), while an excess of the latter reagent leads to the formation of the 4 : 5-dinitro compound. The 5-*nitro* derivative is obtained by direct nitration of acenaphthene in glacial acetic acid solution with concentrated nitric acid (Sachs and Mosebach, Ber. 1911, **44**, 2852). The 1-*nitro* compound, m.p. 151°, is obtained by carefully regulated action of benzoyl nitrate or diacetyl orthonitric acid on acenaphthene (Morgan and Harrison, J.S.C.I. 1930, **49**, 413T). These authors show that the product originally described by Morgan and Sheasby (J.S.C.I. 1925, **44**, 408T) was really impure 3-*nitro* (or 4-) acenaphthene.

Amino-derivatives.—The amino compounds may generally be prepared from the nitro-derivatives by reduction with sodium hyposulphite. 5-*Aminoacenaphthene*, m.p. 108° (Sachs and Mosebach, *l.c.*; Fleischer and Schranz, Ber. 1922, **55** [B], 3253) yields an acetyl compound, m.p. 192°. Crompton and Walker (Proc. Chem. Soc. 1912, **27**, 168) advocate the use of zinc dust and water as the most suitable reducing medium. 1-*Aminoacenaphthene* has m.p. 81·5° (Morgan and Harrison, *l.c.*), while the ω-compound is described below. A number of more complex derivatives are described in the references cited.

Halogen derivatives.—The 4-*chloro* derivative, m.p. 70°, *picrate* m.p. 137°, may be prepared by the action of sulphuryl chloride on acenaphthene in chloroform (Crompton and Walker, J.C.S. 1912, **101**, 958) by direct chlorination of the hydrocarbon in chloroform (Crompton and Cyriax, Proc. Chem. Soc. 1909, **24**, 241) or by treatment of a diazotised solution of 4-aminoacenaphthene with cuprous chloride (Sachs and Mosebach, Ber. 1910, **43**, 2473). The 5-*chloro* compound is produced by chlorination of acenaphthene in methyl or ethyl alcoholic or acetic acid solution in the presence of a trace of iodine or antimony chloride (Paillard and Favarger, Helv. Chim. Acta, 1933, **16**, 614).

The 4-*bromo* and the 4-*iodo*-derivatives have been prepared by the Sandmeyer reaction between the appropriate cuprous halide and a diazotised solution of 4-aminoacenaphthene (Sachs and Mosebach, *l.c.*, 2). They have also been prepared by direct halogenation of the hydrocarbon (Crompton and Walker, J.C.S., *l.c.*). The 4-bromo compound yields a magnesyl derivative from which 4-acenaphthenoic acid is obtained by reaction with CO_2 (Ferrario and Weber, *l.c.*) and 4-cyanoacenaphthene with cyanogen chloride (Grignard, Bellet, and Courtot, Ann. Chim. 1915 [9], **4**, 28).

Sulphonic derivatives.—A monosulphonic acid is obtained by direct sulphonation and its salts and esters have been isolated (Oliveri-Mandalà, Atti R. Accad. Lincei, 1912, **21**, I, 779). Dziewoński and his co-workers (Amer. Chem. Abs. 1924, **18**, 981 ; Ber. 1924, **57** [B], 1531 ; Bull. Acad. Polonaise, 1926, A. 209, 347 ; 1930, A. 518) have studied the orientation of the mono- and disulphonic acids produced under varying conditions, and show that acenaphthene behaves on sulphonation in the same way as naphthalene, substitution taking place in the α-(5)-position at lower and in the β-(3)-position at higher temperatures.

Acetyl derivatives.—The 5-acetyl compound is prepared in the usual way (Graebe, Annalen, 1903, **327**, 91), and Fleischer and Wolff (Ber. 1920, **53** [B], 925) have shown that a diacetyl derivative, m.p. 146°, is produced simultaneously.

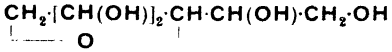
Acenaphthenequinone is best prepared by hydrolysis of its *monoxime* which is obtained by treating acenaphthene with an alkyl nitrite and dry hydrogen chloride (Reissert, Ber. 1911, **44**, 1749). Morgan and Stanley (J.S.C.I. 1925, **44**, 493T) have shown that acenaphthene quinone reacts with phosphorus pentachloride to yield dichloroacenaphthenone; this is reduced by zinc and acetic acid to *acenaphthenone* from which the oxime is formed in the usual way. The oxime is not reduced by mild reducing agents, but with zinc and acetic acid it yields ω-aminoacenaphthene, m.p. 135°, picrate m.p. 260° (decomp.). von Braun and Bayer (Ber. 1926, **59** [B], 920) have shown the presence of acenaphthenol in the product of hydrogenation of the quinone (*see also* Skita, Ber. 1925, **58** [B], 2685).

Two comprehensive reviews of the chemistry of acenaphthene and its derivatives may be found in the Journal of Industrial and Engineering Chemistry (Hahn and Holmes, 1921, **13**, 822 ; F. M. Rowe, 1922, **14**, 80).

ACERDOL. Trade name of calcium permanganate, $Ca(MnO_4)_2$. Recommended for the purification of water.

ACERIDIN. An anthocyanidin from the red leaves of *Acer platanoides*. S. Ionesco (Compt. rend. Soc. Biol. 1927, **96**, 1020, 1022 ; A., 1928, 335).

ACERITOL. An anhydrohexitol, $C_6H_{12}O_5$,



$$CH_2{\cdot}[CH(OH)]_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$$
$$O$$

obtained, together with gallic acid, by the hydrolysis of *Acertannin* from the Korean maple tree *Acer ginnala*. M.p. 142°–143°, $[a]_D^{19}+39°$. A. G. Perkin and Yoshisuke Uyeda (J.C.S. 1922, **121**, 66).

ACER SACCHARINUM, also *A. saccharum*. The sugar maple, a tree growing in N. America, yields a sap which in the spring contains 3–5% saccharose, together with malic, acetic, formic, citric, and traces of fumaric and succinic acids, and other substances. The evaporated sap, *maple sugar*, contains about 85% saccharose, 5% dextrose+lævulose, 9% water, and 0·8% ash. The saccharose is stated to be different from cane sugar. Hortvet, J. Amer. Chem. Soc. 1904, **26**, 1523.

ACERTANNIN, $C_{20}H_{20}O_{13},2H_2O$, and $C_{20}H_{20}O_{13},4H_2O$. A crystalline tannin (*v.* ACERITOL).

ACETALDEHYDE. Synopsis of subject:—

General.—Nomenclature, occurrence, p. 14.

Preparation.—(i) LABORATORY METHODS, p. 14. (ii) FROM ETHYL ALCOHOL, p. 15. (iii) FROM ACETYLENE, p. 16. (iv) MISCELLANEOUS METHODS, p. 19. (v) BIOCHEMICAL PRODUCTION, p. 20.

Reactions and Properties.—(i) PHYSICAL PROPERTIES, p. 20. (ii) CHEMICAL PROPERTIES, GENERAL, p. 21. (iii) REDUCTION TO ETHYL ALCOHOL, p. 22. (iv) OXIDATION TO (*a*) *Acetic acid*, p. 22. (*b*) *Acetone*, p. 25. (v) CONDENSATION AND POLYMERISATION PRODUCTS : (*a*) *Paraldehyde*, p. 25. (*b*) *Metaldehyde*, p. 26. (*c*) *Acetaldol* ; *crotonaldehyde* (and *n-butyl alcohol*), p. 26. (*d*) *Ethyl acetate*, p. 28. (*e*) *Aldehyde resins*, p. 29. (vi) CONDENSATION PRODUCTS WITH AMMONIA AND WITH AMINES, p. 29. (vii) MISCELLANEOUS REACTIONS, p. 29.

Detection and Estimation, p. 30.

Acetaldehyde, aldehyde, ethanal, $CH_3{\cdot}CHO$, is an important simple aliphatic substance which has been known for more than a century and in recent years has attained to great importance as an intermediate in the manufacture of acetic acid, *n*-butyl alcohol, and other products. It was first obtained in an impure form by Scheele in 1774, and known originally as "leichter Sauerstoff-aether" (Döbereiner). It was first investigated in detail by Liebig (Annalen, 1835, **14**, 133 ; 1837, **22**, 273) and from its mode of formation from ethyl alcohol, by removal of two hydrogen atoms :

$$CH_3{\cdot}CH_2{\cdot}OH-H_2=CH_3{\cdot}CHO$$

it was named *aldehyde*, from "*alcohol dehydrogenatus*."

Together with its polymers, metaldehyde and paraldehyde, it is found in the "first runnings" of alcohol refineries and also occurs in crude wood spirit and crude petroleum; it is formed in wines during the process of ageing; in certain circumstances it is produced in the fermentation of alcohol and in animal and vegetable tissues and products (*see* Biochemical production, p. 20).

It may be regarded as the primary dehydration product of the hypothetical *gem*-ethylidene glycol, $CH_3{\cdot}CH(OH)_2$, which is known only in the form of its alkyl ethers, the *Acetals* $CH_3{\cdot}CH(OR)_2$ (*q.v.*), and the ethylidene esters such as ethylidene diacetate, $CH_3{\cdot}CH(OAc)_2$, which may be formed from acetaldehyde and an alcohol or acetic acid, respectively.

Preparation.

(i) LABORATORY METHODS.—The classical method for preparing acetaldehyde is by direct oxidation of ethyl alcohol, for example by air in presence of platinum black (Döbereiner, Gm. **8**, 274), by manganese dioxide and sulphuric acid (Liebig, Annalen, 1835, **14**, 133), by potassium dichromate and sulphuric acid (Städeler, J. 1859, 329). Improved methods and apparatus for converting alcohol into acetaldehyde are described by Boult (B.P. 3998, 1896 ; J.S.C.I. 1896, **15**, 668), Fournier (B.P. 7887, 1897 ; J.S.C.I. 1897, **16**, 695), and Lang (*ibid.* 1903, **22**, 571). Wertheim recommended the oxidation of alcohol with a mixture of sulphuric acid, nitric acid, and sodium bichromate in a stream of carbon dioxide (J. Amer. Chem. Soc. 1913, **35**, 689, 698), whilst Adams and Williams (*ibid.* 1921, **43**, 2420) stated that the yield of aldehyde by the ordinary chromic oxidation is greatly improved by very vigorous stirring of the mixture.

Other methods of preparation are : distillation of calcium acetate with calcium formate (Limpricht, Annalen, 1856, **97**, 369), distillation of lactic acid with manganese dioxide and sulphuric acid (Städeler, Annalen, 1851, **79**, 333), or by the action of dilute sulphuric acid alone :

$$CH_3{\cdot}CH(OH){\cdot}COOH$$
$$=CH_3{\cdot}CHO+H{\cdot}COOH$$

(Erlenmeyer, Zeitsch. f. Chemie, 1868, **4**, 343).

Ethylene oxide, $(CH_2)_2O$, yields acetaldehyde on heating either alone (Nef, Annalen, 1904, **335**, 201), or better in presence of aluminium oxide at 200°C. (Ipatieff and Leontowitsch, Ber. 1903, **36**, 2017).

Acetaldehyde is also produced by treating ethylene glycol with Fenton's reagent, by treating ethylene diamine with nitrous acid (Neuberg and Rewald, Biochem. Z. 1914, **67**, 127), and from pyruvic acid by heating to 150°C. with dilute sulphuric acid (Beilstein and Wiegand, Ber. 1884, **17**, 841) :

$$CH_3{\cdot}CO{\cdot}COOH=CH_3{\cdot}CHO+CO_2\ ;$$

it is also formed on heating an alcoholic solution of an ethyl halide with hexamethylene tetramine or with formaldehyde and ammonia (Fabriques de Laire, B.P. 5533, 1913).

Various aliphatic acids such as succinic, glyceric, maleic, fumaric, tartaric, etc., yield acetaldehyde on treatment with Fenton's reagent in sunlight (Neuberg, Biochem. Z. 1914, **67**, 50).

(ii) COMMERCIAL PRODUCTION FROM ETHYL ALCOHOL.—The most interesting and convenient method, as well as the most important practically, is based on the discovery of Sabatier and Senderens (Compt. rend. 1903, **136**, 738; *cf. also* Bouveault, Bull. Soc. chim. 1908 [iv], **3**, 117) that on passing the vapour of alcohol over a heated metallic catalyst, preferably copper or silver, hydrogen is readily split off with production of acetaldehyde in high yield. Snelling (U.S.P. 1124347) has also claimed a method which consists in passing the vapour of alcohol into a heated porous earthenware tube containing platinum or palladium and drawing off the hydrogen produced which diffuses through the walls of the tubes. It is doubtful if this is a practicable method.

The Sabatier-Senderens method has, however, in recent years become the basis of a very important branch of the organic chemical industry which is demonstrated both by the number of patent applications and by the erection of large works in Great Britain, Germany, the United States and elsewhere, for the manufacture of acetaldehyde from ethyl alcohol.

The effect of various catalysts on the conversion of ethyl alcohol into acetaldehyde has been examined by Engelder (J. Physical Chem. 1917, **21**, 676). Martineau (Compt. rend. 1931, **193**, 1189) has described the production of acetaldehyde by passing a mixture of alcohol and air over a copper-carbon catalyst at 63°C. Patterson and Day (Ind. Eng. Chem. 1934, **26**, 1276) examined the effect of pressure on the reaction, using a silver catalyst, and showed that under atmospheric pressure the optimum yield was at 415°C., while increase of pressure diminished the yield of acetaldehyde. The addition of 0·2% Sm_2O_3 to the silver increased the yield 3–4%.

Kagan and Shneerson examined the yields and obtained 88–96% with a copper catalyst, and 94–97% using a silver catalyst; Kagan and Podurovskaya recommended the use of CuO heated to 900°–950° before reduction and found that the presence of moisture increased the amount of acetic acid formed (J. Appl. Chem. Russia, 1932, **5**, 378, 389).

Calvert (B.P. 132120) claims the oxidation of alcohol to acetaldehyde in an apparatus identical with that described in B.P. 126479 for converting methyl alcohol to formaldehyde. Groombridge, Oxley, and British Celanese Ltd. introduce oxygen and alcohol vapour into the reaction zone through perforated conduits at several points parallel to the line of flow of the reaction mixture (B.P. 391444), whilst water may be removed by cooling the issuing vapours to 40°–70°C., the acetaldehyde being then absorbed directly in glacial acetic acid for oxidation (B.P. 390186, 390211); the same inventors also claim the use of a heat-interchange system in which the reaction bed exchanges heat with a climbing film of cooling liquid (B.P. 390186, 390504).

H. Dreyfus, in a series of patents, describes the use of suitably cooled annular reaction vessels for the oxidation of alcohol to aldehyde (B.P. 390847), the alcohol vapour with air or oxygen and at least its own weight of steam being passed over a silver or copper catalyst (B.P. 389134). The use of silver deposited upon copper as a catalyst is described in B.P. 425550. The water produced in the reaction may be partially removed by treatment with a dehydrating agent such as calcium chloride, etc. (B.P. 389135), or the water and unchanged alcohol may be removed as a ternary mixture by treatment with benzene, the acetaldehyde remaining in vapour form (B.P. 389145), or the moist acetaldehyde vapour may be cooled to 40°–70° to condense the water with only a small amount of acetaldehyde (B.P. 390211); lastly the acetaldehyde itself may be separated by extraction at 100°–150° with a solvent immiscible with water, such as chlorobenzene or paraffin oil (B.P. 390506).

Du Pont de Nemours & Co., Ltd. (with Bond, Smith, and Lazier) claim that on heating ethyl alcohol at 350°/270 atm., in presence of copper containing traces of magnesium or manganese, a mixture is obtained of ethyl acetate, *n*-butyl alcohol, and a lesser amount of acetaldehyde (B.P. 287846); again, on passing alcohol vapour over a catalyst consisting essentially of a basic zinc chromite, copper chromite, manganese chromite, etc., the product consists mainly of acetaldehyde and *n*-butyl alcohol, with lesser amounts of *n*-butyl alcohol (B.P. 313575. *Cf. also* Adkins, Folkers, and Kinsey, J. Amer. Chem. Soc. 1931, **53**, 2714, 4220; Ind. Eng. Chem. 1932, **24**, 314). For the normal process a catalyst is recommended consisting of *electrolytic silver crystals* impregnated with a small amount (*e.g.* 1%) of the oxides of **Al, Cr, Ce, Mo, Th, V, W,** or **Zn** (U.S.P. 1968552).

Scalione and Frazer effect the oxidation of alcohol in presence of free oxygen, by using a metal oxide catalyst which has been prepared by drying below 150° or in a current of neutral gas below 200° (B.P. 166285). Holzverkohlungs Industrie A.-G. claim a 92·3% conversion by using a silver gauze catalyst, a similar method being claimed by Goldschmidt in B.P. 290523, using a silver catalyst at 400°–420°C. Woolcock and Imperial Chemical Industries, Ltd., pass alcohol vapour with air through silver gauze discs contained in a copper tube (B.P. 325105), whilst Boehringer and Soehne recommend the addition of 0·2% of CeO_2 to the reduced copper catalyst. Wiesler, Peake, and British Industrial Solvents, Ltd., obtain acetaldehyde by passing alcohol vapour, steam and air over copper at 420°–440° or silver gauze at 450°–500°, or over the $AgVO_3$ or $Cu(NO_3)_2$ at 350°–400°C. (B.P. 353071). Monsanto Chemical Works claim the use as catalysts of vanadyl zeolites prepared by forming complex silicates containing vanadium in non-exchangeable form, with or without other chemical groups such as boric, phosphoric, tungstic, molybdic, stannic, or plumbic acids, combined with zinc, aluminium, chromium, etc. (B.P. 298142). In B.P. 294037 Fuchs and Holzverkohlungs Industrie A.-G. dry the reaction products by cooling, and then extract the aldehyde by means of a solvent such as aldol, acetic acid, alcohol, etc., the resultant solutions being then polymerised, oxidised, or reduced to yield more aldol, acetic acid, or alcohol respectively.

Young and Carbide and Carbon Chemicals Corpn., in U.S.P. 1977750, pass the vapour of alcohol at 225°–350°C. over a reduced copper catalyst containing not more than 5% of **Cr**, prepared by impregnating an inert carrier with a concentrated solution of 545 parts cupric nitrate and 118 parts chromic nitrate, the mass being dried, roasted at 600°, and then heated at 250°C. in a stream of alcohol vapour.

A large works has been erected on a 45-acre site at Salt End, near Hull, by British Industrial Solvents, Ltd., for the manufacture of glacial acetic acid, *n*-butyl alcohol, etc., from acetaldehyde. Alcohol vapour with air is passed over silver gauze maintained by the heat of the reaction at a dull red heat under rigidly controlled conditions, and very high yields of aldehyde are obtained (*cf.* Chem. Age, Sept. 27, 1930). Unchanged alcohol is fractionated off and returned to the process, the aldehyde being then collected and stored. It is found preferable to employ a number of comparatively small catalytic units rather than a smaller number of larger units, as the process then becomes more flexible and capable of readier control.

(iii) COMMERCIAL PRODUCTION FROM ACETYLENE.—During the last quarter of a century the large-scale manufacture of acetaldehyde from acetylene has become an important branch of applied organic chemistry, mainly as an intermediate for the manufacture of glacial acetic acid and of *n*-butyl alcohol. Works have been erected in Great Britain, Canada, the United States, Germany, Switzerland, and elsewhere, the main consideration being cheap electric power for the manufacture of calcium carbide. More recently also the possibility of producing cheap acetylene by thermal treatment of hydrocarbon oils or gases (*e.g.* in the electric arc) offers a further opportunity for the production of synthetic acetaldehyde from this source.

The basic process depends upon the original discovery of Kutscherow (Ber. 1881, **14**, 1540 ; 1884, **17**, 13), that in the presence of mercury salts, such as mercuric chloride or sulphate, acetylene reacts with water to give acetaldehyde :

$$CH{:}CH + H_2O = CH_3{\cdot}CHO$$

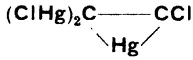
In accordance with the analogy of the formation of vinyl acetate from acetylene and acetic acid (*see* p. 91) :

$$CH{:}CH + HO{\cdot}CO{\cdot}CH_3 = CH_2{:}CH{\cdot}O{\cdot}COCH_3$$

we may assume that the penultimate stage in the synthesis is the formation of the labile vinyl alcohol, which at once isomerises to acetaldehyde :

$$CH{:}CH + H_2O \rightarrow CH_2{:}CH{\cdot}OH \rightarrow CH_3{\cdot}CHO$$

The exact rôle played by the mercury catalyst is still obscure. Hofmann (Ber. 1898, **31**, 2212, 2783 ; 1899, **32**, 874 ; 1904, **37**, 4459 ; 1905, **38**, 663 ; 1908, **41**, 312 ; 1909, **42**, 4232) and Biltz and others (Ber. 1904, **37**, 4417 ; 1905, **38**, 133 ; Annalen, 1914, **404**, 219) investigated the white precipitate formed by passing acetylene into an aqueous solution of mercuric chloride. Hofmann considers that the first product of the reaction is a substance having the constitutional formula :



which is rapidly hydrolysed by water to trichloromercuriacetaldehyde, $(ClHg)_3C{\cdot}CHO$. Biltz and his co-workers have shown that the white precipitate almost certainly has the constitution of trichloromercuriacetaldehyde, but they regard the evidence for the formation of Hofmann's intermediate compound as unsatisfactory.

Brame (J.C.S. 1905, **87**, 427), however, has shown that a white substance observed by Biginelli (Chem. Zentr. 1898, i, 926) to be formed in small quantities by the action of acetylene on mercuric chloride in dilute hydrochloric acid solution can be obtained in a pure crystalline condition ; it is an additive compound and has the constitution :

$$ClHg{\cdot}CH : CHCl$$

and is decomposed by water, yielding acetaldehyde, free hydrochloric acid, and a little trichloromercuriacetaldehyde.

Chapman and Jenkins (J.C.S. 1919, **115**, 847) and Jenkins (J.C.S. 1921, **119**, 747) have confirmed Brame's results and have succeeded in preparing the additive compound in quantity (50 g. from 72 g. of mercuric chloride) by the action of acetylene on a saturated solution of mercuric chloride in absolute alcohol containing hydrogen chloride. It is a crystalline compound, m.p. 129°, and soluble in most organic solvents. (*See also* article on ACETYLENE.) Decker has discussed the theoretical basis of the hydrolysis of vinyl ethers to acetaldehyde (Helv. Chim. Acta, 1930, **13**, 666).

(*a*) *Process.*—The first British Patent dealing with the subject is by the Chem. Fabrik Griesheim Elektron (B.P. 29073, 1910), in which a process is claimed consisting in passing acetylene into a solution of a mercury salt in an organic or inorganic acid below 70°C. (*e.g.* sulphuric, phosphoric, acetic, chloracetic acids). The use of 45% sulphuric acid mixed with mercuric oxide is recommended. Owing to the war and the unexpected importance of processes for the manufacture of acetaldehyde, for conversion to acetic acid and thence to acetone, N. Grünstein's original German Patent Application (G. 40228 of July 2, 1913) remained in abeyance for 13 years and the complete patent G.P. 425665, was only granted on Feb. 11, 1926, with extension of " life " ; it was later acquired by I.G. Farbenind. A.-G. This patent covered the process for the production of acetaldehyde by passing a continuous stream of acetylene through dilute sulphuric acid containing a mercury catalyst. A general discussion of the priority of earlier patents is given in Z. angew. Chem. 1918, **31**, 148, 180. Chem. Fabrik Griesheim Elektron (B.P. 15669, 1914) claim the use of a 20–35% aqueous solution of sulphuric, phosphoric, or an organic sulphonic acid, etc., containing a mercury salt, the temperature being kept below the boiling-point. The Consort. f. Elektrochem. Ind. G.m.b.H. describe a modification consisting in passing acetylene through sulphuric acid solutions of mercury oxide, containing less than 60 parts SO_4 per 1,000 parts of water, at temperatures above 70°C. (B.P. 6000, 1913). The aldehyde distils off as it is formed and mercury is deposited at the bottom of the liquid ; the patent also claims an electrolytic process for re-oxidising the mercury which is gradually formed by reduction during the process. In B.P. 16848, of 1913, the same firm describe a process in which the acetaldehyde is swept out of the solution as it is formed, by a stream of excess acetylene, the aldehyde being removed and the residual gas recirculated (*see also* B.P. 208689). Fr. Bayer and Co. (B.P. 6527, 1914) claimed a similar process, the sulphuric acid being replaced by an organic sulphonic acid, *e.g.* benzene sulphonic acid (di- or tri-sulphonic acids), etc., the object being to avoid the condensation and polymerisation of the acetaldehyde which is caused by the prolonged action of stronger acids, such as mineral acids.

Boiteau in B.P. 15919 of 1914 recommends the production of a catalytic liquid by dissolving a mercuric salt in a suitable solvent and then forming the sulphate *in situ*, by the addition of sulphuric acid ; the process is, however, mainly concerned with the production of ethylidene diacetate.

A further improvement claimed by the Consort. f. Elektrochem. Ind. G.m.b.H. (B.P. 16957, 1914) consists in so adjusting the rate of flow of the acetylene and the temperature of the reaction vessel that the heat evolved by the reaction is balanced by the heat lost by evaporation of water, thus attaining a state of approximate thermal equilibrium, fresh water being added continuously to keep the volume constant. The use of thermally insulated and water-jacketed vessels is recommended. A further patent (B.P. 5132, 1915) is concerned mainly with the use of solvents such as glacial acetic acid, ethylidene diacetate, etc., in presence of mercuric oxide and a strong acid, water being added continuously in the theoretical proportions. A continuous process using 6% sulphuric acid containing mercuric oxide in suspension, at 40°–65°C., and at pressures slightly above atmospheric, is claimed by Matheson and Canadian Electroproducts, Ltd., in B.P. 132557 ; continuity is maintained by the periodic addition of water, acid and mercuric oxide.

Dreyfus (B.P. 105064) recommends the use of sulphuric acid of 5–20% at a temperature below 60°C., the acetylene being led in at such a rate that all is absorbed. The acetylene is introduced slowly at first until all the mercury compound present (5–20%) has become grey or greyish-black. The acetaldehyde formed may be removed periodically either by distillation or by extraction with solvents such as tetrachlorethane, etc., water being added at intervals. In B.P. 106483 Dreyfus modifies his process by using sulphuric acid of more than 20% and extracting the acetaldehyde with suitable solvents.

The removal of acetaldehyde from mixed reaction products by extraction with a solvent such as methyl-*cyclo*hexanone, benzene, etc., in stages, at or above its boiling-point, is claimed by Usines de Melles in B.P. 380928.

The formation of undesirable by-products is largely prevented, according to Hibbert and Morton (U.S.P. 1213486, 1213487, 1247270 ; Canad. P. 181655–6–7), by the introduction of a salt of a weak acid, *e.g.* a borate, into the catalytic mercury solution ; the absorption of the acetylene and distillation of the acetaldehyde is stated to be more complete. A claim is also made for the use of several catalytic baths arranged in series to ensure complete absorption. In B.P. 260305 the Consort. f. Elektrochem. Ind. G.m.b.H. recommend the catalytic hydration of acetylene in presence of a solvent for the gas, such as phenols, ketones, acetals, esters, etc.

I.G. Farbenind. A.-G. claim the catalytic production of acetaldehyde from acetylene in presence of mercuric salts, at pressures exceeding 2 atm., the method being especially applicable to mixtures containing dilute acetylene obtained by the thermal decomposition of hydrocarbons (B.P. 278324) ; they also claim the use of a catalyst comprising a solution of an alkali-metal bi-sulphate, containing a mercury salt, or a salt of a heavy metal of the 1st or the 8th groups of the periodic system, such as copper or iron (B.P. 312716), whilst in B.P. 319542 a claim is made for the use of a solution of mercuric and ammonium salts for effecting the hydration ; the use of slightly increased pressures, temperatures above 85°C., and an excess of acetylene is recommended in B.P. 349022. The same inventors claim the use of heated concentrated aqueous solutions of salts having a slightly acid reaction, such as the chlorides of zinc, chromium, magnesium, calcium or ferric iron, in presence of mercuric oxide or uranyl nitrate (B.P. 313864) ; this last process may be modified by the use of increased pressure with the addition of a small amount of water, insufficient to destroy the acid reaction but enough to lower the boiling-point to at least 4°C. below the boiling-point of the corresponding saturated solution (B.P. 393690).

(*b*) *Regeneration and Recovery of Mercury Catalyst.*—One great difficulty found in the early years of this branch of chemical industry lies in the fact that the mercury catalyst gradually becomes reduced and is deposited as a heavy tarry sludge at the bottom of the vessel, the solution thus gradually losing its catalytic activity.

Hilditch and Crosfield suggested overcoming this trouble by reoxidising the sludge to mercuric oxide by the periodic addition of small amounts of suitable oxidising agents such as manganates, permanganates or hydrogen peroxide (B.P. 124702, 125926) ; or by lead peroxide, manganese dioxide, or ceric oxide (B.P. 131084).

The Soc. Chem. Ind. in Basle regenerate the catalyst by electrolysis in presence of a suitable oxygen carrier such as an iron salt (B.P. 130138) ; more generally, however, the formation of mercury sludge is prevented or delayed by the introduction into the catalytic liquor of oxidising agents such as chromic acid, chromates, or in particular ferric salts (Meister, Lucius, and Brüning, B.P. 24153, 1914; G.P. 293070; U.S.P. 1151928, 1151929). Riley and Imperial Chemical Industries, Ltd., recommend the use as a catalyst of a mercury salt solution containing ferric sulphate, a portion of the liquor being continuously removed, reoxidised by oxygen, and returned to the process (B.P. 346883). Alternatively, the catalyst may be prepared by mixing mercury with a suitable oxidizing agent such as ferric oxide, and then adding dilute sulphuric acid (Soc. Anon. de Prod. Chim. Établ. Maletra, B.P. 140785). A continuous regeneration process using electrolytic oxidation with a platinum anode and mercury cathode is described by the Chem. Fabr. Griesheim-Elektron in B.P. 143891. Again, the spent reaction liquor of B.P. 140785 (*v.s.*) may be regenerated by first removing all aldehyde present, precipitating the mercury from the solution by means of iron filings, and finally reoxidising the ferrous salt solution by electrolysis (Soc. Anon. de Prod. Chim. Établ. Maletra, B.P. 165085).

As an alternative the sludge itself may be removed and treated in various ways to revivify it or to recover the mercury: thus the Chem. Fabr. Griesheim-Elektron advise carbonising the residue by heat or else mixing the sludge with caustic lye and electrolysing (B.P. 10140, 1915). Matheson also recommends letting the sludge settle, neutralising with alkali and heating to 125°C.; the liquid mercury is then run off, the residue being ground up and carbonised by heating it to 100°-500°C. (B.P. 132559). Riley, Rowell, and Imperial Chemical Industries, Ltd., recover the mercury by treating the sludge with chlorine and removing the resultant mercuric chloride solution (B.P. 332106); whilst Hirst, Rowell, and Imperial Chemical Industries, Ltd., suggest treating the sludge with strong nitric acid and then adding concentrated sulphuric acid to precipitate mercuric and ferric sulphates (B.P. 309888). The Chem. Fabr. Worms A.-G. advise heating the spent catalytic material with iron powder or other reducing agent to 200°C. for several hours (B.P. 156187).

The preparation of the requisite mercuric oxide for the production of the fresh catalyst may be carried out electrolytically, according to Matheson (B.P. 132560; *cf.* Canad. Chem. J. 1919, **3**, 259); mercury and dilute aqueous caustic soda are placed in a large cast-iron pan, 6 ft. in diameter and 15 ins. high, oxidation being effected with current density of about 55 amps. per sq. ft., at 8–10 volts, using an iron or nickel cathode (*cf. also* Daniell and Elektrizitätswerk Lonza, G.P. 311173).

(*c*) *Use of Other Catalysts.*—A number of attempts have been made to effect the hydration of acetylene by the passage of steam and acetylene over heated dry catalysts which may or may not contain non-volatile mercury compounds; the Deuts. Gold- u. Silber-Scheidenanstalt vorm. Roessler pass a mixture of acetylene and steam over contact agents such as molybdic acid on asbestos, at high temperatures (B.P. 107584). The Chemische Fabrik Rhenania suggest passing the same mixture over bog iron ore at 400°–420°C., or over hydrated iron oxide, bauxite, hydrated aluminium silicates, or compounds of copper, nickel, chromium, vanadium, etc. (B.P. 109983; *cf. also* B.P. 107585).

I.G. Farbenind. A.-G. claim the production of acetaldehyde by passing acetylene and steam over non-volatile mercuric compounds such as the phosphate, vanadate or sulphate in presence, if desired, of silver or tin vanadates; in presence of air acetic acid is formed (B.P. 321241). Again, the catalyst may consist of silico-tungstic acid deposited on clay, or basic zinc tungstate (B.P. 329867), or it may comprise alumina activated by dehydrogenating catalysts such as cadmium oxide, zinc oxide, cadmium sulphide, or zinc sulphide together with the corresponding chromates, tungstates, molybdates, etc. (B.P. 332635). Acetaldehyde may also be obtained by passing a mixture of approximately equal volumes of acetylene and steam over a catalyst comprising, for example, zinc oxide, manganese dioxide and chromic acid, at 180°–200°C. (Mittasch, Pier, Winkler, and I.G. Farbenind. A.-G., G.P. 415686). In a later patent by the same firm it is proposed to pass a mixture of acetylene, steam and oxygen, saturated with mercury vapour at 200°–260°C., over a mixed catalyst such as mercuric phosphate with other heavy metal oxides and/or salts, deposited on pumice, clay, etc. (B.P. 364255). Wohl (B.P. 154579) recommends passing a mixture of air, steam, and acetylene over a heavy metal salt which is stable below 300°–400°C., such as basic zinc chloride, basic zinc vanadate, molybdate or chromate; the product consists of acetaldehyde with some acetic acid. A similar process of the Consort. f. Elektrochem. Ind. A.-G. (B.P. 373893) consists in passing acetylene and steam through molten zinc chloride, with or without the addition of ($BaSO_4$+ZnO) or a mixture of oxides such as CeO_2, ZnO, Cr_2O_3, MnO, BaO, TiO_2, etc., at 300°–450°C., the exit vapours being then passed over a heated solid catalyst to complete the conversion, if desired. In a modified process acetylene and oxygen, together with small amounts of nitrogen oxides and in substantial absence of steam, are passed over heated quartz or porcelain at 287°–407°, to yield acetaldehyde and acetic acid (Gutehoffnungshütte Oberhausen A.-G., B.P. 376045). Horsley, Tanner, and Imperial Chemical Industries, Ltd., recommend the use of a catalyst composed of zinc oxide and a molybdate, at 300°–350°C. (B.P. 334427), or of bismuth salts such as the phosphate or molybdate, using a large excess of steam in the process (B.P. 344638), whilst by the use of cadmium phosphate at 300°–400°C. acetaldehyde and crotonaldehyde are produced (B.P. 346288), or the catalyst may consist of boron trioxide and phosphoric acid ("boron phosphate") at 200°–400°C. (B.P. 351016). Traun's Forschungslaboratorium proposes to obtain acetaldehyde by hydrating acetylene with steam at 250°–300°C./5–10 atm. in presence of small quantities of acetic, sulphuric, or organic sulphonic acids, etc. (B.P. 156152), whilst I.G. Farbenind. A.-G. propose passing gases containing acetylene through concentrated aqueous solutions of neutral salts at 140°, the salts having an acid reaction in concentrated solutions (*e.g.*

salts of zinc, cadmium, chromium, etc.), and the residual gases are then further catalytically hydrated, for example, by passage at 300°–400°C. over a mixture of the oxides of aluminium, tungsten, and zinc (B.P. 313864, 425069).

I.G. Farbenind. A.-G., in B.P. 340787, claim a process for the purification, prior to conversion to acetaldehyde, of acetylene-rich gases produced thermo-electrically, by passing the gases over porous carbon or silica gel (*cf. also* B.P. 386052 ; *vide* article ACETYLENE) ; they also claim the use of mercuric phosphate, at temperatures above 120°C., for the hydration of crude dilute acetylene, or the use of silver vanadate on active carbon at 250°C. or over (B.P. 304855). The production of acetaldehyde from dilute mixtures containing 2–10% of acetylene, by washing the gases in a counter-current with a suitable mercuric sulphate catalyst solution, is claimed by Hirst and Imperial Chemical Industries, Ltd., in B.P. 302515. The same problem is also dealt with in B.P. 414347 (void) (Murphree and Standard Oil Co.).

In a somewhat different category are the following :—I.G. Farbenind. A.-G. claim the production of acetaldehyde by passing ethylene oxide over a catalyst obtained by heating together copper carbonate and magnesium ammonium phosphate, etc. (B.P. 331185) ; the same firm in B.P. 334223 describes the manufacture of ethyl alcohol by leading acetylene, saturated with water vapour at 90°C., first over zinc oxide or silica gel, etc., at 380°C., and then, admixed with hydrogen, over nickel at 200°C.

A general description of preparing acetaldehyde from acetylene is given by Thommen in Chem.-Ztg. 1934, **58**, 797.

Benson and Cadenhead note the occurrence of diacetyl, of $CH_3·CO·CH(OH)·CH_3$, and of other potentially valuable by-products in the synthesis of acetaldehyde from acetylene (J.S.C.I. 1934, **54**, 40T).

(*d*) *Apparatus and Plant.*—The use of acid-resisting silicon-iron vessels for the process is recommended by Dreyfus in B.P. 115899. Comp. de Prod. Chim. d'Alais describe the production of acetaldehyde from acetylene in an apparatus in which the reaction liquid is subjected continuously to a vacuum so as to remove the acetaldehyde as it is formed (B.P. 130650). As originally carried out on the large scale at the Shawinigan works of Canadian Electro-products, Ltd., acetylene gas was led into dilute sulphuric acid containing mercuric oxide in suspension, the oxide being added continuously and the acetaldehyde carried off in the excess of acetylene used (Canad. Chem. J. 1919, **3**, 260).

Soller, Hotz, and the British Cellulose and Chemical Co. recommend that parts of the apparatus exposed to the action of sulphuric acid shall be of lead, coated electrolytically with lead peroxide (B.P. 151086) (*cf. also* B.P. 105064, Dreyfus). In B.P. 155776 and 217747 Brutkus describes apparatus for producing acetaldehyde from acetylene and water vapour in a type of compressor in which they are brought to reaction during compression strokes, temperature and pressure being maintained constant by injection of a spray of water. In B.P. 294227 (void) (Kárpáti and Hübsch a plant is described in which the acetylene and the absorbing solution are maintained in separate circulatory systems having the reaction chamber in common. I.G. Farbenind. A.-G. in B.P. 299234 (grant of patent refused) claim the use of chromium-nickel steel for the construction or lining of the apparatus, whilst in B.P. 298108 Harter describes a form of vessel including a rotating fan, or impeller, made of, or coated with, platinum so that a stream of acetylene, steam, and oxygen may be impelled through the vessel and caused to react with production of acetaldehyde.

(iv) MISCELLANEOUS METHODS.—Small amounts of acetaldehyde are formed, together with ethylene glycol, on hydrolysing *s*-dichlorethane with water and barium carbonate at 160°–180°C. for 1 hour (Askenasy and Heller, U.S.P. 1928240).

Emeléus (J.C.S. 1929, 1733) states that acetaldehyde is formed to the extent of about 10% in the phosphorescent cold flame of ether, whilst Marie and Lejeune (Anal. Fís. Quím. 1930, **27**, 447) describe a method of electrolysing ether in presence of perchloric acid which affords acetaldehyde in 30% yield.

H. Dreyfus claims the production of mixtures of acetic acid, acetaldehyde and acetone by passing a mixture of methane, carbon monoxide, and carbon dioxide under pressure (*e.g.* 12–50 atm.) and below 500° over various catalysts such as copper, iron, nickel, cobalt, palladium, etc. (B.P. 226248, 337409–10). Walker and the Empire Gas and Fuel Co. also claim the production of methanol, formaldehyde and acetaldehyde by a similar process from natural gas, coal gas, shale gas, oil gas, etc. (B.P. 295356, void). In B.P. 304623 the I.G. Farbenind. A.-G. claim the production of acetaldehyde, formaldehyde and formic acid from hydrocarbons and air under the influence of the silent electric discharge ; the same firm also notes the production of acetaldehyde as a by-product obtained on passing hydrocarbon mixtures, together with steam and air, over catalysts such as oxides of manganese, vanadium, chromium, aluminium, etc., at 500°–800°C. (B.P. 305603). In B.P. 267925 the same firm describes the preparation of acetaldehyde by passing carbon monoxide and acetic acid vapour at 200°–550° over a mixture of iron and cobalt ; whilst Dreyfus reduces waste or dilute acetic acid to acetaldehyde by catalytic reduction with hydrogen, using finely divided nickel, iron, zinc, tin, lead, pumice, etc., as catalysts (B.P. 273810). The formation of acetaldehyde as a by-product during the catalytic oxidation of various gaseous hydrocarbons at 350°–600° is noted in B.P. 321494 (Arnold and Standard Oil Development Co., Ltd.), whilst Gutehoffnungshütte Oberhausen A.-G. note the production of acetaldehyde and formaldehyde by treating a mixture of methane and carbon dioxide with a high-frequency field of 20,000 volts or over, at cycles greater than 10,000 per second (B.P. 353455).

Behrens describes the production of acetaldehyde by mixing the gases obtained by distilling coal, wood, turf, etc., with 5–6% of carbon dioxide and heating the mixture for some time (G.P. 276764).

Aldehyde is also formed to some extent by heating charcoal saturated with acetylene to 350°C. with water (Degriz, Ann. Chim. Phys. 1894 [vii], **3**, 216).

I.G. Farbenind. A.-G. claim the production of acetaldehyde by passing ethylene oxide over a reduced catalyst such as one prepared from copper carbonate and magnesium ammonium phosphate, at 180°–200°C. (B.P. 331185). A more unusual claim is made by Curme consisting in passing ethylene into a solution of a mercuric salt, the compound produced being then subjected to anodic oxidation to produce acetaldehyde, which is removed continuously by distillation (U.S.P. 1315543, 1315546).

(v) Production and Occurrence in Biochemical Processes.—As noted above, acetaldehyde is formed to some extent during the ageing of wine (Trillat, Compt. rend. 1903, **136**, 171 ; Ann. Inst. Pasteur, 1908, **22**, 704, 753, 876 ; Bull. Soc. chim. 1909 [iv], **5**, 546, 550 ; 1910 [iv], **7**, 71). It occurs in the fermentation products of alcohol, under certain conditions (Trillat, Compt. rend. 1908, **146**, 645, Trillat and Sauton, *ibid.* 1908, **146**, 996 ; Kayser and Demolon, *ibid.* **146**, 783 ; Trillat and Sauton, Bull. Soc. chim. 1910 [iv], **7**, 244 ; Ann. Inst. Pasteur, 1910, **24**, 302 ; Kostytschev, Z. physiol. Chem. 1912, **79**, 130 ; 1912, **83**, 93 ; 1914, **89**, 367 ; 1914, **92**, 402 ; Biochem. Z. 1914, **64**, 237 ; Kostytschev and Hübbenet, Z. physiol. Chem. 1912, **79**, 359 ; 1913, **85**, 408 ; Neuby and Kerb, Biochem. Z. 1912, **43**, 494 ; 1914, **64**, 251 ; Ber. 1914, **47**, 2730 ; Grey, Biochem. J. 1913, **7**, 359 ; Buchner, Langheld, and Skraup, Ber. 1914, **47**, 2550 ; Müller-Thurgau and Osterwalder, Amer. Chem. Abstr. 1916, 2274, 2474).

According to Battelli and Stern (Biochem. Z. 1910, **28**, 145) acetaldehyde is produced in animal tissues by oxidation of alcohol, through the action of alcoholase. It occurs in poplar blossoms (Kostytschev, Hübbenet, and Shelounov, Z. physiol. Chem. 1912, **83**, 105), and by oxidation of certain substances such as rhamnose (Rosenthaler, Arch. Pharm. 1913, **251**, 587). Kerbosch showed the presence of traces of acetaldehyde in the latex of *Hevea braziliensis* (Rec. trav. chim. 1915, **34**, 235). It is possibly also a degradation product of glucose in the animal body, and may be reduced to alcohol by the liver (*cf.* Embden and Baldes, Biochem. Z. 1912, **45**, 157).

By the use of dimethyl-dihydroresorcinol as a reagent Neuberg and Reinfurth (Biochem. Z. 1920, **106**, 281 ; 1921, **115**, 282) showed that the acetaldehyde formed in the alcoholic fermentation of sugar can, in the presence of neutral sodium sulphite, be accumulated to the extent of 73·5% of the theoretical (Biochem. Z. 1918, **89**, 365 ; J. Inst. Brew. **25**, 181). (*See also* Annual Reports on the Progress of Applied Chemistry, 1920, 426, and Cohen, Biochem. Z. 1920, **112**, 139 ; Neuberg, Nord, and Wolff, *ibid.* **112**, 144.) In B.P. 164034 Cocking and Lilly claim that by yeast fermentation of sugar in presence of alkali sulphite and bisulphite, the acetaldehyde produced along with the alcohol and glycerol is taken up by the bisulphite as it is formed. In B.P. 291146 Bücher claims the recovery of acetaldehyde in a continuous process for manufacturing yeast in a closed vessel, the gases liberated being treated with solvents or absorbents. According to Neuberg and Windisch (Biochem. Z. 1925, **166**, 454), in the formation of acetic acid by the bacterial oxidation of alcohol, acetaldehyde is formed by direct oxidation, and is then further transformed under the influence of aldehydase into acetic acid and alcohol. The presence of acetaldehyde in growing plants is discussed by Neuberg and Gottschalk (Biochem. Z. 1925, **160**, 256), and by Bodnár, Szepessy, and Ferenczy (Biochem. Z. 1925, **165**, 16). According to Kostytschev (Z. physiol. Chem. 1920, **111**, 126, 132) large amounts of acetaldehyde are formed when alcoholic fermentation is effected by dead yeast cells in presence of zinc or cadmium salts. Gottschalk (Z. physiol. Chem. 1927, **168**, 136) has shown the formation of acetaldehyde as an intermediate stage in the degradation of pentoses (*cf.* Rosenthaler. *supra*). Hartley and Fisher (J. Agric. Res. 1927, **35**, 983) have shown that acetaldehyde is a normal metabolic product of healthy pears, but pears having more than 15 mg. of aldehyde per 100 g. of fresh tissue develop scald and core breakdown. Traut and Tomkins have shown that the sound condition of stored fruit may be prolonged in an atmosphere containing small proportions of acetaldehyde (1/250 to 1/1000), but the margin of safety between concentrations effective in preventing mould growth and those causing injury to fruit is small (J. Counc. Sci. Ind. Res. Australia, 1931, **4**, 6 ; *cf.* B. 1931, 513).

The formation of acetaldehyde during pancreatic digestion is noted by Hoffmeister (Z. physiol. Chem. 1932, **205**, 183), whilst the rate of disappearance of the aldehyde in muscle extracts is greatly increased by the presence of hexose-diphosphate (Barrenscheen and Braun, Biochem. Z. 1932, **253**, 414). The conversion of acetaldehyde into alcohol or acetic acid under aerobic conditions is discussed by Windisch (Biochem. Z. 1932, **253**, 466). Zuckerkandl and Messiner-Klebermass have shown that the reduction of acetaldehyde to alcohol by the action of yeast is dependent upon the presence of glucose or glycogen (Biochem. Z. 1932, **255**, 330). The formation of acetaldehyde by the action of boiling aqueous alkalis on proteins has been noted by Riesser, Hanson, and Nagel (Z. physiol. Chem. 1931, **196**, 201).

Reactions and Properties.

(i) Physical Properties.—Acetaldehyde is a mobile, colourless liquid, b.p. 20·8°C., m.p. −120·7°C., d^0 0·80092 (Kopp, Annalen, 1847, **64**, 214), d^{10} 0·79509, d^{13} 0·79138, d^{16} 0·78761 (Perkin, J.C.S. 1884, **45**, 475).

It possesses a pungent suffocating odour at high concentrations but in great dilution has a not unpleasing apple-like odour. It is highly inflammable and burns with a feebly luminous flame. Acetaldehyde is miscible in all proportions with alcohol, ether or water, and may be separated from its aqueous solution by the addition of calcium chloride ; it is probable that in dilute aqueous solution it exists as *aldehydrol, ethylidene glycol,*

$$CH_3\cdot CH(OH)_2$$

(Perkin, J.C.S., 1887, **51**, 815 ; Homfray, *ibid.* 1905, **87**, 1434). Its viscosity at 15°C. is 0·02456 (Hatcher and Mason, Canad. J. Res. 1933, **8**, 402). The refractive index n_D^{20} is 1·33157 (Landolt) ; for its value in the gaseous state, *see* Lowery (Phil. Mag. 1932 [vii], **14**, 743). For electric moments, *see* Zahn (Physikal. Z. 1932, **33**, 686).

The structure of acetaldehyde has been examined by Schou (Compt. rend. 1927, **184**, 1452) by means of its ultra-violet absorption curves which indicate the presence of a small amount of an enolic form.

(ii) Chemical Properties.—On heating with aqueous alkalis, so-called *aldehyde-resin* is formed as a brown amorphous gum (*cf.* Weidenbusch, Annalen, 1848, **66**, 153 ; Lederer, Monatsh. 1901, **22**, 536). This property has latterly been utilised for the production of technically useful resins.

Sodium amalgam converts aldehyde into ethyl alcohol, together with a small amount of $\beta\gamma$-butylene glycol, which is also formed by the action of magnesium amalgam (Meunier, Compt. rend. 1902, **134**, 473 ; Tischtschenko and Grigoréeff, J. Russ. Phys. Chem. Soc. 1906, **38**, 540 ; Voronkoff, *ibid.* 547 ; Kekulé, Annalen, 1872, **162**, 310). Acetaldehyde reacts violently with sodium, producing the compound $CH_2:CH\cdot ONa$, which rapidly polymerises to a brown substance ; if the reaction takes place in presence of benzoyl chloride aldehydroaldol benzoate, $C_{13}H_{16}O_4$, is produced, m.p. 86°–87°C. (Freer, Amer. Chem. J. 1896, **18**, 552 ; Annalen, 1896, **293**, 326).

Phosphorus pentachloride reacts with acetaldehyde to form ethylidene dichloride :

$$CH_3\cdot CHO+PCl_5=CH_3\cdot CHCl_2+POCl_3$$

(Geuther, Annalen, 1858, **105**, 323) ; with potassium cyanide it yields alanine and α-iminodipropionic acid (Franzen and Ryser, J. pr. Chem. 1913, **88**, 293). Acetaldehyde reacts in the normal manner with hydrogen cyanide to form *acetaldehyde cyanhydrin*, which can be hydrolysed to *lactic acid :*

$$CH_3\cdot CHO\xrightarrow{HCN}CH_3\cdot CH(OH)\cdot CN$$
$$\xrightarrow{H_2O}CH_3\cdot CH(OH)\cdot COOH$$

(Imperial Chemical Industries, Ltd., B.P. 341961) ; in presence of ethyl alcohol, ethyl lactate is obtained (Matheson, Blaikie, and Canadian Electro-Products, Ltd., B.P. 257907 ; *cf. also* Tiemann, Ber. 1881, **14**, 1965 ; Strecker, Annalen, 1854, **91**, 349 ; Erlenmeyer and Parravant, *ibid.* 1880, **200**, 120).

Substitution Products.—The halogen substitution products of acetaldehyde are mostly of little technical interest ; on passing chlorine into the aldehyde at 10°C., metaldehyde and paraldehyde (*q.v.*) are first formed and these subsequently yield substitution products, of which chloral is the chief, butyl chloral and dichloracetaldehyde being formed in smaller amounts (Wurtz, Annalen, 1857, **102**, 93 ; Wurtz and Voigt (Bull. Soc. chim. 1872 [ii], **17**, 402 ; Pinner, Annalen, 1875, **179**, 21 ; Freundler, Bull. Soc. chim. 1907 [iv], **1**, 66 ; Compt. rend. 1906, **143**, 682).

Monochloracetaldehyde, which cannot be made by direct chlorination of the aldehyde, is best prepared from *ethyl αβ-dichlorethyl ether* ; this is converted into *chloracetaldehyde alcoholate* by the action of water and calcium carbonate, and alcohol removed by heating with oxalic acid (Fritsch and Schumacher, Annalen, 1894, **279**, 307) :

$$CH_2Cl\cdot CHCl\cdot O\cdot C_2H_5$$
$$\xrightarrow{H_2O}CH_2Cl\cdot CH(OH)\cdot O\cdot C_2H_5$$
$$\longrightarrow CH_2Cl\cdot CHO+C_2H_5\cdot OH$$

It is a mobile, very pungent liquid, b.p. 85°, and forms a hydrate, $2C_2H_3OCl+H_2O$—possibly $CH_2Cl\cdot CH(OH)\cdot O\cdot CH(OH)\cdot CH_2Cl$—m.p. 43°–50°. Monochloracetaldehyde readily polymerises to a translucent amorphous mass.

Dichloracetaldehyde, $CHCl_2\cdot CHO$, b.p. 89·5°–90·5°C. (*cf.* Grimaux and Adams, Bull. Soc. chim. 1880 [ii], **34**, 29 ; Wohl and Roth, Ber. 1907, **40**, 212). For condensation products with anisic acid, *p*-nitroanisole, and *p*-hydroxybenzoic acid, *see* Chattaway and Farinholt (J.C.S. 1931, 1828).

Trichloracetaldehyde, $CCl_3\cdot CHO$, is the most important of the halogenated aldehydes and was first prepared by Liebig in 1832 from the chlorination products of alcohol (Annalen, 1832, **1**, 189) under the name of *chloral* (*q.v.*). It forms a hydrate, *chloral hydrate*, which is used as a soporific.

For detailed references to halogen derivatives of acetaldehyde, *see* Meyer and Jacobson, Lehrbuch der organischen Chemie, I (ii), p. 865 *et seq.*, Leipzig, 1913.

Chloroform may be prepared by the action of bleaching powder upon acetaldehyde in presence of water (Utheim, B.P. 116094).

Additive Compounds.—Acetaldehyde shows a pronounced tendency to yield polymers and condensation products, and also unites directly with many substances to form additive compounds.

(*a*) *Compounds with metallic salts.*—The following are known : with mercuric sulphate, $SO_4:(HgO)_2:HgC_2H_4O$ (Denigès, Compt. rend. 1899, **128**, 429) ; with mercuric nitrate, $C_2Hg_2NO_4H,[NO_3\cdot Hg\cdot C(:Hg)\cdot CHO]$ (Hofmann, Ber. 1898, **31**, 2212) ; with mercuric acetate in alkaline soln., $CMeHO,HgO$ (Lasserre, J. Pharm. 1905, **22**, 246). With gold chloride acetaldehyde yields a coloured colloidal gold solution (Garbowski, Ber. 1903, **36**, 1215) ; with magnesium bromide, $MgBr_2,3CH_3\cdot CHO$ (Menschutkin, Z. anorg. Chem. 1907, **53**, 26) ; with calcium cyanide it forms $C_6H_{10}O_6N_2Ca_3$ (Franzen and Ryser, J. pr. Chem. 1913, **88**, 2929). A compound with potassium cyanide is referred to in B.P. 19463 of 1913.

(*b*) *Compounds with alkaline bisulphites.*—Acetaldehyde forms definite crystalline compounds when dissolved in concentrated aqueous solutions of alkali bisulphites ; the *potassium salt*, $C_2H_4O\cdot KHSO_3$, crystallises in indistinct needles ; the *sodium salt*, $C_2H_4O\cdot NaHSO_3 + \frac{1}{2}H_2O$, forms fine needles or nacreous platelets. The *ammonium* compound has the formula $C_2H_4(OH)\cdot SO_2\cdot NH_2$. These salts are very sparingly soluble in excess of the bisulphite solutions and form a convenient method for isolating and purifying acetaldehyde, which may be obtained from them by distillation with an acid, an alkaline carbonate, or alkali nitrites. With hyposulphites in neutral or acid solution acetaldehyde hyposulphite is obtained, $2CH_3\cdot CHO\cdot M_2S_2O_4$ (F.P. 360306 ; J.S.C.I. 1906, **25**, 475) ; by varying the conditions the sulphoxylates, $CH_3\cdot CH_2\cdot SO_3M$, may be obtained (G.P. 180529).

(*c*) *Compound with ammonia.*—By leading dry ammonia into an ethereal solution of acetaldehyde the well-known compound *aldehyde-ammonia* is formed, $C_2H_4O\cdot NH_3$, which crystallises in large rhombohedra, m.p. 70°–80°C., b.p. 100°C., and is decomposed into its constituents on distillation with dilute acids. When hydrogen sulphide is passed through a suspension of aldehyde-ammonia in ether a crystalline substance, $SH\cdot CHMe\cdot NH\cdot CHMe\cdot OH$, is obtained, m.p. 60°–63°C. (Chabrié, Compt. rend. Soc. Biol. 1896, **3**, 72). (See also *Condensation Products with Amines, infra.*)

(*d*) *Compounds with acids.*—Under certain conditions acetaldehyde reacts with acids or acid anhydrides to form ethylidene esters, *e.g.* ethylidene acetate, $CH_3\cdot CH(O\cdot CO\cdot CH_3)_2$ (*v.* Acetals). For other compounds with acids, *see* Geuther, Annalen, 1858, **106**, 249 ; Lieben, *ibid.* 336 ; 1875, **178**, 43 ; Rübenkamp, *ibid.* 1884, **225**, 2791 ; Schiff, Ber. 1876, **9**, **304** ; Ponzio, J. pr. Chem. 1896 [ii], **53**, 431 ; Schroeter, Ber. 1898, **31**, 2189 ; Annalen, 1899, **303**, 114 ; Delépine, Compt. rend. 1901, **133**, 876 ; McIntosh, Amer. Chem. J. 1902, **28**, 588 ; Wegscheider and Späth, Chem. Zentr. 1910, i, 1421.

(*e*) *Compounds with alcohols.*—Acetaldehyde condenses with alcohols in presence of suitable catalysts to afford *acetals*, *e.g.* ethylacetal, $CH_3\cdot CH(OC_2H_5)_2$ (*v.* Acetals).

(iii) Reduction to Alcohol.—Acetaldehyde is readily reduced to ethyl alcohol and from the practical standpoint the main difficulty is one of economics rather than of chemistry. In presence of reduced nickel, hydrogen reduces acetaldehyde to ethyl alcohol with good yield (Sabatier and Senderens, Compt. rend. 1903, **137**, 301). Various practical modifications have been suggested : thus, Dreyfus carries out the reduction by passing the mixture of hydrogen and acetaldehyde vapour through reaction vessels or tubes containing suitable catalysts such as platinised asbestos, copper, iron, chromium, nickel, vanadium, etc. (or their oxides) at temperatures between 20°–400°C. (B.P. 108856). The Elektrizitätswerk Lonza (Swiss Pat. 74129, 1917) claims the production of ethyl alcohol by passage of acetaldehyde vapour and a large excess of hydrogen over a heated catalyst (*cf. also* B.P. 120163, 128929). Alternatively the reduction may be effected electrolytically by leading acetaldehyde into the cathode chamber of an acid cell (Chem. Fabr Griesheim-Elektron, G.P. 328342), whilst I.G. Farbenind. A.-G. obtain alcohol by passing acetylene and steam first over a condensation catalyst such as zinc oxide or silica gel at 380°C., and then, admixed with hydrogen, over a reducing catalyst such as nickel at 200°C. (B.P. 334223 ; *cf. also* G.P. 384351, Badische Anilin- u. Soda-Fabrik). Bancroft and George (J. Physical Chem. 1931, **35**, 2194) have investigated the catalytic equilibrium between acetaldehyde and alcohol ; using a finely divided nickel catalyst the equilibrium value for the reaction $CH_3\cdot CH_2\cdot OH \rightleftharpoons CH_3\cdot CHO + H_2$ (at 140°–145°), lies at about 3% of acetaldehyde. Water vapour was found to activate the nickel surface for both reactions. Platinised asbestos did not catalyse either reaction at 140°–145° nor could the aldehyde be reduced electrolytically to alcohol using a platinum cathode. The cathodic reduction in dilute lithium chloride solution was investigated by Smoler (Coll. Czech. Chem. Comm. 1930, **2**, 699).

The technical aspects of the question have been discussed in the Chemical Trade Journal, 1918, 283, and Chem.-Ztg. 1918, **42**, 311. During the war it is understood that the Elektrizitätswerk Lonza were granted a concession by the Swiss Government to manufacture 7,000 tons of ethyl alcohol a year from calcium carbide, at their works at Visp (Ind. Eng. Chem. 1917, **9**, 903), but it is not known to what extent this project was fulfilled. For the production of 1 ton of alcohol by this process about 1 ton of calcium carbide is necessary and 500 cu. m. of hydrogen, the former requiring some 8,000 kw.-hours for its manufacture and the latter about 3,000 kw.-hours. In addition, each ton of alcohol requires 2,500 kg. of coal and 4,000 kg. of limestone (Chem. Ind. 1917, **40**, 335). In view of the fact that it is now commercially practicable to prepare acetaldehyde by the converse process from alcohol obtained by the more usual fermentation process, it does not seem likely that the synthesis of alcohol from calcium carbide via acetylene and acetaldehyde is possible under present-day conditions, except as an emergency measure.

(iv) Oxidation to Acetic Acid.—Acetaldehyde is easily oxidised to acetic acid, for instance with potassium permanganate :

$$CH_3\cdot CHO + O \rightarrow CH_3\cdot COOH$$

although in presence of excess of potassium hydroxide, oxalic acid and carbonic acids are also formed (Denis, Amer. Chem. J. 1907, **38**, 561). Again, in the oxidation of alcohol to acetaldehyde with acidified bichromate solution, excess of the oxidising agent leads to the formation of acetic acid. Fry and Schultze have examined the action of fused alkali upon acetaldehyde and obtained a 90% conversion to sodium acetate at 250°C. :

$$CH_3\cdot CHO + NaOH = CH_3\cdot COONa + H_2$$

but at higher temperatures methane and sodium carbonate are formed :

$$CH_3\cdot CHO + 2NaOH = H_2 + CH_4 + Na_2CO_3$$

(J. Amer. Chem. Soc. 1926, **48**, 958).

The slow oxidation of acetaldehyde at 50 atmospheres pressure between 340°–430°C. has been investigated by Newitt and Szego (Proc. Roy. Soc. 1935 [A], **147**, 555), the results supporting the hydroxylation theory of combustion; the inflammation of mixtures of acetaldehyde and air between 200°–350°C. has been examined by Prettre (Compt. rend. 1931, **193**, 240). Bodenstein has made a detailed examination of the slow combustion of acetaldehyde vapour and oxygen at 55°–99°C./70 mm., and found that, usually after a period of induction, the process consisted in the activation of acetaldehyde molecules which then combined with molecular oxygen to form activated molecules of peracetic acid and the energy of these was then transferred to further aldehyde molecules (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, III, 18; A. 1931, 572).

The oxidation of acetaldehyde by ceric sulphate in dilute acid solution at 80°C. leads to the formation of formic acid, carbon dioxide, glyoxylic acid, and glycollaldehyde (Conant and Tongberg, J. Biol. Chem. 1930, **88**, 701). Treatment of acetaldehyde with acidified hydrogen peroxide at 95°C. yields mainly methane and hydrogen (Bezzi, Gazzetta, 1933, **63**, 345). Peace (J. Amer. Chem. Soc. 1933, **55**, 2753) has also examined the reaction between acetaldehyde and oxygen at 90°–150°C. under reduced pressure, the product being mainly acetic acid. The reaction was autocatalytic, the initial rate being proportional to the square of the concentration of aldehyde but independent of the oxygen concentration; the formation of peroxides as "chain carriers" is indicated (*cf. also* Hatcher, Steacie, and Howland, Canad. J. Res. 1932, **7**, 149).

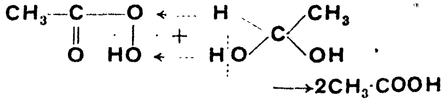
Technically, it has been found possible to oxidise acetaldehyde almost quantitatively by means of oxygen or air, in presence of suitable catalysts. The reaction appears to take place in two stages, (*a*) the formation of peracetic acid:

$$CH_3{\cdot}CHO + O_2 = CH_3{\cdot}CO{\cdot}O{\cdot}OH$$

which then (*b*) reacts with further acetaldehyde to form acetic acid:

$$CH_3{\cdot}CO{\cdot}O{\cdot}OH + CH_3{\cdot}CHO = 2CH_3{\cdot}COOH$$

and one purpose of the catalysts usually employed is to ensure the speedy conversion of the dangerously explosive per-acid to the end-product. It has been found that peracetic acid and acetaldehyde do not react in the dry state but do so in the presence of water, the per-acid acting presumably as a hydrogen acceptor towards the hydrated aldehyde:



(Hatcher, Steacie, and Howland, Canad. J. Res. 1931, **5**, 648; Wieland, Annalen, 1932, **495**, 284 (*see also* Bowen and Tietz, J.C.S. 1930, **234**)). The general subject of the technical conversion of acetaldehyde to acetic acid has been reviewed by Thommen (Chem.-Ztg. 1935, **59**, 133).

Two types of process have been investigated and patented: (1) where air and acetaldehyde are passed over a heated catalyst, and (2) where air or oxygen is passed into liquid acetaldehyde containing a dissolved catalyst (usually colloidal manganic acetate).

(1) *Vapour Phase Oxidation.*—A mixture of acetaldehyde vapour with air or oxygen may be passed through heated tubes containing contact substances such as platinised asbestos at a temperature above the boiling-point of the aldehyde, the mixed gases being pre-heated by a heat interchanger similar to that used in a catalytic sulphuric acid converter (Dreyfus, B.P. 105065). In a later patent (B.P. 108459) Dreyfus recommends the use of excess air at 150°–250°C., in presence or absence of a catalyst such as platinum, copper, copper oxide, chromic oxide, uranium oxide, vanadium oxide, cerium oxide, iron, pumice, etc., or again, the requisite mixture of aldehyde vapour and air may be obtained by passing air through liquid acetaldehyde, or the aldehyde may be vaporised by a current of air entering the bottom of the reaction chamber itself (Dreyfus, B.P. 110545). The temperature of the liquid aldehyde, or of the air, is regulated so as to control the composition of the mixture, or the acetaldehyde may be diluted, for instance with acetic acid, to effect the same purpose. The liquid acetic acid formed collects in a suitable part of the apparatus and flows away, whilst the issuing gas containing unchanged acetaldehyde is recovered and recirculated (F.P. 479656 and additions 20201, 20202). The use of kieselguhr as a catalyst is claimed by Fr. Bayer and Co. (G.P. 299782), of a granular mixture of coke and alumina at 100°C. (Soc. des Usines du Rhône, B.P. 126279), of calcium and magnesium phosphates, with or without small amounts of lime, silica, and fluorides (Dreyfus, B.P. 154680).

The production of acetic acid direct from acetylene, steam and air in presence of suitable catalysts no doubt involves the intermediate formation of acetaldehyde (*cf.* Chem. Fabr. Rhenania, B.P. 109983; I.G. Farbenind. A.-G. B.P. 364255; *see* article ACETYLENE).

The Chem. Fabr. Griesheim-Elektron recommend the addition of acetic acid, acetic anhydride or chloracetic acid to the aldehyde and then passing the liquid or vapours, with oxygen or air, through tubes or towers packed with glass or clay, preferably using a catalyst such as vanadium pentoxide, uranium oxide, or roasted ferrosoferric oxide, Fe_3O_4 (B.P. 17424, 1911); in an addition to this patent (B.P. 8076, 1912), an improvement is claimed which consists in treating small quantities of acetaldehyde with oxygen in vessels, tubes, towers, etc., until the greater part is oxidised to acetic acid, then adding further quantities of aldehyde and passing a stronger current of oxygen, preferably in the presence of a catalyst. Utheim (B.P. 116279) recommends the use of oxygen under pressure, the acetaldehyde being supplied to the oxygen in limited quantities in a confined space, *e.g.* in a number of narrow tubes, with cooling. The oxidation may also take place in suitable tubes or towers by means of air or oxygen, in absence of a catalyst, the product being continuously heated to destroy any peracetic acid present (B.P. 130651). Hibbert (U.S.P. 1230899, Can. P. 178237) recommends the use of a wood charcoal previously saturated with strong acetic acid, to promote the reaction between acetaldehyde and oxygen, using it as a packing for towers through which the mixture is passed; when working at 45° a 70% acid in 90% yield is obtained.

An electrolytic process for oxidising paraldehyde to acetic acid in 10% sulphuric acid containing salts of manganese, cerium, molybdenum, or vanadium is claimed in B.P. 124195, 131600 (Soc. Anon. des Aciéries et Forges de Firminy).

(2) *Liquid Phase Oxidation.*—In B.P. 16849 of 1913, the Consort. f. Elektrochem. Ind. G.m.b.H. describe the production of peracetic acid by treating acetaldehyde with oxygen at a low temperature in absence of moisture or manganese compounds. On allowing the peracetic acid to attain normal temperature it is decomposed by the remaining aldehyde to form acetic acid. In view of the known dangerous properties of peracetic acid, however, this process can only be regarded as a safeguarding patent. The next patent by the same firm (B.P. 17016, 1913) claims the production of acetic acid by oxidising acetaldehyde by means of air or oxygen in presence of a catalytic manganese salt. The catalyst may be obtained by introducing permanganates into the aldehyde, when reduction takes place to a catalytically active colloidal brown solution containing manganic acetate. The action of manganese catalysts has been examined by Kagan and Lubarsky (J. Physical Chem. 1935, **39**, 837), who suggest that the action of the catalyst may be to hasten the decomposition of an intermediate peroxide, produced by the addition of peracetic acid to acetaldehyde, as well as to break up peracetic acid into acetic acid and active oxygen. It is suggested that the intermediate peroxide has the structure HO·CHMe·O·O·COMe, and decomposes relatively slowly in absence of a catalyst (Kagan and Lubarsky, *ibid.* 1935, **39**, 847). In a later patent the Consortium replace permanganates by an organic salt of manganese such as the formate, acetate, benzoate, etc. (B.P. 7418, 1914).

The use of manganese compounds as catalysts is referred to in several other patents by various inventors. Dreyfus describes the oxidation of acetaldehyde in the liquid phase by means of air or oxygen at 0°–10°C., at atmospheric pressure, in presence of ferric oxide, ferric acetate, etc., with vigorous agitation (B.P. 130035). The ferric oxide employed may be prepared by precipitation from solution followed by ignition at 310°–500°C., and small amounts of sodium acetate may also be present (B.P. 156916).

Oxidation may be effected by passing air or oxygen in excess into acetaldehyde under pressure and in presence of a catalyst such as manganese acetate, *e.g.* at an initial temperature of 20°–25° raised gradually to 65°C., under 5 atm. pressure (Matheson, B.P. 132558). The pressure vessel used may be provided with a reflux condenser which returns the condensed aldehyde below the surface of the liquid (Matheson, B.P. 154368). The formation of the dangerous peracetic acid may be prevented by the use of solid salts containing water of crystallisation such as acetates of nickel, cobalt, manganese, or chromium; or alums, ferrous sulphate, sodium acetate, etc. (Traun's Forschungslaboratorium G.m.b.H., B.P. 156146).

Rowell, Hirst, and Imperial Chemical Industries, Ltd., describe a continuous process for the oxidation in which the vapour of acetaldehyde with air, or oxygen, is passed up a tower down which flows an acetic acid solution containing 0·2% of manganese acetate and 0·002% cobalt acetate (B.P. 304350, 308937), whilst Rowell and Imperial Chemical Industries, Ltd., claim the use of a very finely divided stream of air or oxygen (for instance, forced through a porous plate) for effecting the oxidation (B.P. 319433). In B.P. 347323 Holzverkohlungs Industrie A.-G. prevent the accumulation of dangerous amounts of peracetic acid by the use of at least 50% excess of oxygen at 55°–80°C. and 1·5 atm., whilst the Nippon Chissohiriyo Kabushiki Kaisha lessen the danger of explosion by filling the gas space above the reaction liquid with an inert gas such as nitrogen or carbon dioxide, etc. (B.P. 359878).

Means for maintaining a constant pressure in the oxidation system is claimed by the Deuts. Gold- u. Silber-Scheideanstalt vorm. Roessler (B.P. 380887).

The oxidation may also be effected on the counter-current system in a series of vessels, the aldehyde-acetic acid liquor flowing in one direction and the oxygen in the other (B.P. 350874). Challis, Groombridge, Oxley, and British Celanese, Ltd., claim the use of manganese acetate as a catalyst (B.P. 367863). The maintenance of the concentration of the acid at about 70%, in presence of various catalysts, is described in B.P. 368348, and the recovery of escaping aldehyde by scrubbing with acetic acid, the scrub liquors being returned to the reaction kettle, in B.P. 366022.

The oxidation may also be effected continuously in a vertical column of acetic acid, acetaldehyde and air (or oxygen) being supplied at the bottom whilst cold acetic acid and a suitable catalyst (*e.g.* salts of Mn, Cu, Co, Ni, Cr, Fe, V, etc.) are added continuously to the top. The temperature in the column may vary from 25°–40° at the top to 30°–100° at the bottom (I.G. Farbenind. A.-G., B.P. 405719). Again, acetaldehyde dissolved in glacial acetic acid, or an inert medium, may be treated with air or oxygen containing ozone at 50°–58°C., and the resultant acid removed continuously (A.-G. f. Stickstoffdünger, B.P. 426875).

Paraldehyde can be oxidised to acetic acid by electrolysis, using 10% sulphuric acid as electrolyte on which floats a layer of paraldehyde, an anode of magnetite or platinum being employed, in presence of salts of manganese, cerium, molybdenum, or vanadium (Soc. Anon. des Aciéries et Forges de Firminy, B.P. 124195).

In an earlier patent (B.P. 10377, 1914), Meister, Lucius and Brüning asserted that greatly improved results were obtainable by passing the air or oxygen under pressure into acetaldehyde in the presence of such suitable catalysts as ferric oxide, ceric oxide, vanadium pentoxide, chromic oxide, or platinum black; the following table shows the percentage of the theoretical yield of acetic acid obtained under certain conditions:

	With catalyst.	With pressure.	With pressure + catalyst.
After 1 hour .	4%	5%	35%
,, 5 hours .	16%	20%	95%

The use of ferric acetate as a suitable catalyst for the oxidation was claimed by Dreyfus in B.P. 130035, whilst in B.P. 17018, 1913, the Consort. f. Elektrochem. Ind. G.m.b.H. described a modification of the process of B.P. 16849, 1913, using as catalysts salts of chromium, cobalt, iron, uranium, and vanadium.

For the problem of preparing acetic acid in one stage from acetylene and oxygen, without isolation of the acetaldehyde, *see* ACETYLENE.

On heating acetaldehyde vapour to 150°-500°C. in presence of a dehydrogenating catalyst such as nickel, copper, or zinc at 5-50 atm. *keten* is formed, which may be used directly for acetylations, or it can be treated with water to yield acetic acid (Dreyfus, B.P. 273622), whilst on passing keten into glacial acetic acid, acetic anhydride is formed directly (Nightingale and Ketoid Co., B.P. 237575).

Little has been published regarding the technical production of acetic acid by the oxidation of acetaldehyde, but it has now become the standard commercial method for the manufacture of the glacial acetic acid required in immense quantities for the manufacture of cellulose acetate,' and the world production probably exceeds 100,000 tons per annum. Thus, about 1921 the output at Shawinigan was stated to be about 20,000 tons of acid by the acetylene route, whilst the Farbwerk Hoechst produced 10,000–12,000 tons. At the present day (1936) the capacity at Shawinigan is stated to be 50,000 tons per annum with an output of 36,000 tons, whilst at Salt End, near Hull, the capacity is some 10,000 tons per annum, via ethyl alcohol (*cf.* Canad. Chem. J. 1919, **3**, 260; J.S.C.I. 1921, 343R). According to Cadenhead (Canad. Chem. J. 1919, **3**, 268) 1 ton of calcium carbide produces about half a ton of acetic acid, though this figure may have been improved since that date.

OXIDATION TO ACETONE.—The possibility of obtaining acetone directly from acetaldehyde has recently been carefully examined.

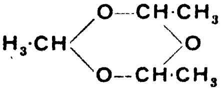
Zelinski, Uschakov, Michailov, and Arbuzov have shown that a 96% conversion of acetaldehyde into acetone can be effected by passing the vapour of the former, together with water vapour, over a 7 : 3 mixture of ferric oxide and manganese dioxide at 400°C. (under similar conditions acetylene itself gave an 88% yield of acetone) (J. Appl. Chem. Russ. 1934, **7**, 83; J. Chem. Ind. Russ. 1933, **10**, 63). Kagan, Sobolev, and Lubarski (Ber. 1935, **68** [B] 1140) postulate the intermediate formation of ethyl acetate on passing acetaldehyde over a Cu, $(Cu+Cr_2O_3)$ or $(ZnO+Cr_2O_3)$ catalyst at 300°–350°C., the ester is then transformed to acetone above 400°C.

Dreyfus claims the production of acetone by passing the vapour of acetaldehyde preferably at 350°–550°C., over one of a variety of mixed catalysts comprising a salt of an alkaline earth metal together with ferric oxide, cupric oxide, etc. (B.P. 340233), whilst Du Pont de Nemours and Co., in B.P. 428871, obtain similar results by passing acetaldehyde vapour, diluted with nitrogen, carbon dioxide, methane, etc., at 400°–500° over a catalyst composed of oxygenated derivatives of certain metals, *e.g.* mixed hydroxides of chromium and nickel, carbonates of zinc, uranium, etc.

Yamada (J. Soc. Chem. Ind. Japan, 1933, **36**, 193; A. 1933, 937) states that a mixture of zinc oxide with calcium oxide is more effective than either catalyst alone for converting a mixture of acetaldehyde and steam into acetone.

(v) POLYMERISATION AND CONDENSATION PRODUCTS. — (*a*) *Paraldehyde.* — Acetaldehyde readily polymerises in the presence of various reagents such as sulphuric acid, phosgene, zinc chloride, hydrogen chloride, sulphur dioxide, halogens, etc., two polymers being obtained, the relative amounts of which depend mainly upon the temperature. When the reaction occurs at low temperatures the main product is the solid *metaldehyde*, $(C_2H_4O)_n$ (n=4 or 6) and liquid *paraldehyde* at ordinary or higher temperatures. Paraldehyde, $(C_2H_1O)_3$, is readily prepared by the addition of a drop of concentrated sulphuric acid to acetaldehyde, the liquid boiling up at once with almost explosive violence; the product can be purified either by freezing out below 0°C., and removing the liquid portion, or by washing with dilute soda solution, drying over calcium chloride, and rectifying. Polymerisation is also caused by halogen hydracids; in this case addition products are formed, such as $(C_2H_4O)_3 \cdot 3HCl$, m.p. −18°C., $(C_2H_4O)_3 \cdot 3HBr$, m.p. −15°C., $(C_2H_4O)_3 \cdot 3HI$, liquid below −32°C. The rate of polymerisation has been examined by Hatcher and Brodie, who found that in benzene solution, in presence of phosphoric acid, equilibrium was attained with 94·3% of paraldehyde (Canad. Res. J. 1931, **4**, 574). Hnizda and Brown (J. Physical Chem. 1932, **36**, 2842) have also examined the reaction.

Paraldehyde is a clear, mobile, colourless liquid of pleasant odour and sharp taste, b.p. 124°C., m.p. 12·5°C., d^{15} 0·9984 (Hatcher and Kay, Canad. Res. J. 1932, **7**, 337). It possesses the same molecular weight in solution and in the vapour phase. It is sparingly soluble in water, 100 vols. water dissolving 12 parts paraldehyde at 13°C., the solubility diminishing on warming. It shows no characteristic aldehydic reactions: thus, it does not reduce ammoniacal silver nitrate, does not resinify on heating with aqueous potash, and does not unite with ammonia or bisulphites. Its formula is therefore assumed to be:



It is completely depolymerised on warming with a little sulphuric acid; many other reagents produce a similar effect, which may also occur on long standing. Owing to its ease of depolymerisation paraldehyde can frequently replace acetaldehyde in reactions in which the volatility of the latter is inconvenient. Thus, paraldehyde condenses with diacetonamine to form vinyl-diacetonamine, and with aniline to form quinaldine ; it sets free iodine from alkali iodides ; it is not readily attacked by pure nitric acid but is easily oxidised in presence of nitrous acid. Paraldehyde is used to some extent as a soporific.

Smits and de Leeuw assume the existence of an equilibrium of a pseudo-ternary system, of (acetaldehyde metaldehyde-paraldehyde), the values for the different components varying according to the catalyst (Proc. K. Akad. Wetensch. Amsterdam, 1910, **13**, 318 ; A. 1910, 815 ; Z. physikal. Chem. 1911, **77**, 268 ; *cf.* Hatcher and Brodie, Canad. Res. J. 1931, **4**, 574). Bromination of paraldehyde at low temperatures yields *bromo-paracetaldehyde*, m.p. 27·5°C., which decomposes at 130°C. into bromoacetaldehyde (Stepanov, Preobraschenski, and Schtschukina, Ber. 1926, **59** [B], 2533).

(*b*) *Metaldehyde* may be prepared by treating acetaldehyde with dry hydrogen chloride at low temperatures (Patterson and Holmes, J.C.S. 1935, 904). The following catalysts have also been recommended for treatment of acetaldehyde below 10°C., titanium chloride, lithium bromide, halides of sodium, potassium, calcium, strontium, aluminium, cerium, etc., together with hydrochloric acid, ferric chloride, etc., or salts of organic bases with strong acids may be used (Elektrizitätswerk Lonza A.-G., B.P. 198576, 235867). Metaldehyde has been marketed in recent years as a convenient smokeless solid fuel for use in small domestic appliances, model steam-engines, etc., under the name of " Meta " fuel (Elektrizitätswerk Lonza A.-G., B.P. 144589 ; U.S.P. 1407101). It may be stabilised for use as a fuel by the addition of small amounts of ammonium carbonate (B.P. 189074). To obviate any possible dangers of poisoning it has been proposed to admix metaldehyde fuel tablets with capsaicin or similar substances (B.P. 371196).

Metaldehyde crystallises in needles or tetragonal prisms and sublimes without melting at 112°-115°C., d^{15} 1·120–1·127 (Hatcher and Kay, Canad. Res. J. 1932, **7**, 337). It is reconverted completely into acetaldehyde when heated in sealed tubes at 120°C. Metaldehyde is quite stable when pure, it exists in one form only, it is not termolecular but is quadrimolecular in phenol solution (Hantzsch and Oechslin, Ber. 1907, **40**, 4341).

The crystalline structure of metaldehyde has been examined by Hassel and Mark (Z. physikal. Chem. 1924, **111**, 357).

(*c*) *Aldol, Crotonaldehyde* (and *n-Butyl alcohol*). —Acetaldehyde is readily condensed by a variety of reagents to *acetaldol* (aldol) :

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$

which forms a thick oily liquid, d^0 1·121, d^{16} 1·1094, b.p. 83°/20 mm. On prolonged standing it forms crystalline "*Paraldol,*" m.p. 82°C. It is capable of being distilled *in vacuo* or under reduced pressure, but on distillation under normal pressure, particularly in presence of a dehydration catalyst such as hydrochloric acid or sulphuric acid, it easily loses water to form *crotonaldehyde* :

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH : CH{\cdot}CHO + H_2O$$

The same result may be attained more simply by distillation in superheated steam.

In recent years this process has become of considerable technical importance, as the crotonaldehyde can be reduced catalytically to *n*-butyl alcohol. It will be convenient, therefore, to deal with aldol and crotonaldehyde separately.

(1) *Aldol* is formed from acetaldehyde under the influence of both acid and alkaline condensing agents such as cold dilute hydrochloric acid, aqueous zinc chloride, or aqueous potassium carbonate. The following methods have been patented : the use of alkali carbonates, borates, phosphates, cyanides, or hydroxides (Du Pont de Nemours Powder Co., Ltd., B.P. 17259, 1911) ; alkaline salts, or sodium ethoxide, may be dissolved in a substantially water-free solvent such as ethyl alcohol (B.P. 22621, 1912 ; Swiss P. 64932 ; U.S.P. 1151113). The use of alkali or alkaline-earth metal or their alloys or amalgams, or of metallic alkoxide or cyanides soluble in acetaldehyde, in absence of water, is claimed by the Consort. f. Elektrochem. Ind. G.m.b.H. (B.P. 19463, 1913). Suitable organo-metallic compounds to act as catalysts are formed by adding alkali or alkaline-earth metals to acetaldehyde in absence of water (G.P. 269996). The use of lime, strontia, calcium carbide, etc., if desired, in presence of a trace of water, is recommended by Grünstein (B.P. 101636 ; U.S.P. 1234156). Hibbert suggests the addition of potash or caustic soda to a solution of acetaldehyde in gasoline at – 10°C. (U.S.P. 1086048). The use of a mixture of calcium chloride and sodium hydroxide solutions is claimed by Wacker and Ges. f. Elektrochem. Ind. G.m.b.H. (G.P. Appl. W. 64787). The use of an alkaline condensing agent insoluble in an organic solvent, such as caustic alkalis, alkaline-earth oxides, cyanides, or carbides, etc., in presence of water, is claimed by Grünstein (B.P. 147119). Another method of effecting the condensation is by the slow addition of aqueous barium hydroxide, with subsequent removal of the barium by means of carbon dioxide (Elektrizitätswerk Lonza, B.P. 179523), or conversely by the gradual addition of acetaldehyde to a sludge of barium hydroxide (Silberrad, B.P. 273776). Again, a mixture of acetaldehyde and 1·25% sodium hydroxide solution may be passed through a series of cooled tubes (I.G. Farbenind. A.-G., B.P. 298349). An ingenious method of removing the heat of reaction consists in utilising the endothermic dehydration of sodium sulphate decahydrate which is mixed with a little anhydrous sodium carbonate, or of sodium carbonate decahydrate (Boake and Townsend, B.P. 352056) ; the use of sodium carbonate with a little water (less than 25% of the weight of the soda) has also been claimed (Durrans and Lewis, B.P. 353413). Horsley and Imperial Chemical Industries, Ltd., recommend the use of a neutral or faintly alkaline solution where the hydroxyl ion concentration does not exceed 0·00001 *N* ; *e.g.*

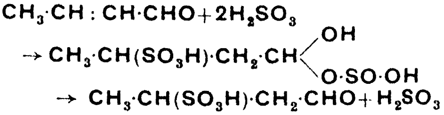
acetic acid buffered by sodium acetate, in absence of oxygen (B.P. 313466). An apparatus for effecting the condensation to aldol, in which the heat-exchanging elements are partly embedded in the catalyst, is described by Jaeger and the Seldon Co. (B.P. 306883).

The reduction of aldol by aluminium amalgam is referred to in B.P. 17259, 1911 (Du Pont de Nemours Powder Co.), the product being *αγ*-butylene glycol. The use of hydrogen in presence of suitable catalysts, *e.g.* metals of the 1st and 8th periodic groups, etc., is claimed by I.G. Farbenind. A.-G. in several patents (B.P. 309200, 311671, 328083, 338807, 348248). The main purpose of such processes appears to lie in the fact that on dehydration with suitable catalysts 1 : 3-butadiene is formed :

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$
$$\xrightarrow{H_2} CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$$
$$\xrightarrow{-2H_2O} CH_2{=}CH\;\;CH{=}CH_2$$

which may be polymerised to a form of synthetic rubber (*see* RUBBER, SYNTHETIC).

(2) *Crotonaldehyde* (*β-methyl-acrolein*). — As already noted above, aldol is readily dehydrated to crotonaldehyde by heating either alone or with suitable catalysts. It is a mobile, pungent liquid, possessing lachrymatory properties, b.p. 104°–105°C., d_4^{14} 0·8593 ; the *oxime* has m.p. 119°–120°C. It reacts with sulphurous acid to form a sulphurous acid derivative of butyraldehyde-*β*-sulphonic acid, from which the latter acid is formed on boiling the aqueous solution :



$$CH_3{\cdot}CH:CH{\cdot}CHO+2H_2SO_3$$
$$\rightarrow CH_3{\cdot}CH(SO_3H){\cdot}CH_2{\cdot}CH\begin{cases}OH\\ O{\cdot}SO{\cdot}OH\end{cases}$$
$$\rightarrow CH_3{\cdot}CH(SO_3H){\cdot}CH_2{\cdot}CHO+H_2SO_3$$

With chlorine it reacts in the cold to form *αβ*-dichlorbutyraldehyde,

$$CH_3{\cdot}CHCl{\cdot}CHCl{\cdot}CHO,$$

but prolonged chlorination without cooling leads to the formation of *αβ*-dichlorobutyryl chloride, $CH_3{\cdot}CHCl{\cdot}CHCl{\cdot}COCl$. With alcohol and dry hydrogen chloride in the cold it forms *β*-chlorobutyraldehyde diethylacetal,

$$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CH(OEt)_2.$$

A certain amount of crotonaldehyde is generally formed as a by-product in the synthesis of acetaldehyde, but a number of processes have been described for its manufacture. Sabatier and Gaudion describe the crotonisation of aldehyde by treatment with thorium, titanium, or uranium oxides at 300°C. (Compt. rend. 1918, **166**, 632). Crotonaldehyde is formed by subjecting aldol to a temperature below 165°C. in an inert atmosphere (B.P. 242521, U.S.P. 1585096). It is also obtained, together with aldol, by treating acetaldehyde with highly dilute caustic alkali solution, and fractionating the product in a nitrogen atmosphere (Luscher and Elektrizitätswerk Lonza, B.P. 270764) ; a similar method being claimed by Soc. Anon. des Distilleries des Deux Sèvres (B.P. 274488), the crotonaldehyde separating as a binary mixture with water. In the manufacture of crotonaldehyde from aldol a small amount of an inorganic acid may be added to the aldol before heating, to decompose its content of organic alkali salts (Holzverkohlungs Ind. A.-G., B.P. 320210). Crotonaldehyde and its polymerisation products suitable for denaturing alcohol are produced as by-products during the electrolytic reduction of aldehyde to ethanol in an acid electrolyte, by raising the temperature slowly to 70°–80°C. (Pascal, B.P. 140527 ; *cf. also* Johansson, B.P. 185126).

Crotonaldehyde may be prepared conveniently from aldol in a continuous or semi-continuous manner by distilling an aqueous solution of aldol (preferably containing more than 3 parts of water to 1 of aldol), in presence of inorganic salts such as sodium sulphate and carbonate (B.P. 352056), keeping the liquid substantially neutral, an azeotropic mixture of crotonaldehyde and water distilling off (Bloomfield and Townsend, B.P. 370252).

The auto-oxidation of crotonaldehyde may be suppressed by the addition of 0·001% of quinol (Moureau and Dufraisse, Compt. rend. 1922, **175**, 127).

The following may be noted as minor technical uses for crotonaldehyde : oxidation to crotonic acid in glacial acetic acid solution in presence of a manganese salt, and subsequent removal of the solvent by distillation (Elektrizitätswerk Lonza, B.P. 165728) ; oxidation to maleic acid and anhydride at 250°–380°C. in presence of oxides or salts of vanadium or molybdenum (I.G. Farbenind. A.-G., B.P. 369963); or crotonaldehyde may be condensed with methyl alcohol in presence of sulphuric acid to alkyloxyaldehydes and acetals such as methoxybutaldehyde (Wacker, Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 347943, 348001).

The chief use for crotonaldehyde is for reduction to *n*-butyl alcohol, an operation which is now an important branch of chemical industry.

(3) n-*Butyl alcohol* (*Butanol*).—Crotonaldehyde may be readily reduced to *n*-butyl alcohol, for example by passing the vapour mixed with hydrogen over a heated copper catalyst (Badische Anilin- und Soda-Fabrik, G.P. 350048, 362537, 407837, 416906), or over a mixed copper and nickel oxide catalyst at 100°–120°, using a considerable excess of hydrogen (Horsley and Imperial Chemical Industries, Ltd., B.P. 321253):

$$MeCH:CH{\cdot}CHO+4H$$
$$=MeCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

Young and the Carbide and Carbon Chemicals Corporation recommend passing the vapour of crotonaldehyde with excess of hydrogen over a nickel catalyst containing 1–5% of Cr_2O_3, at about 180°C., and 30 lbs. pressure (U.S.P. 1966157). The process of reduction has been investigated by Kagan, Ljubarski, and Fedorov (J. Appl. Chem. Russ. 1934, 7, 135 ; B. 1934, 567).

The *n*-butyl alcohol so produced may be purified by treatment with chlorine, bromine, or their hypo-acids (I.G. Farbenind. A.-G., B.P. 312512). Propylene may be recovered from the surplus hydrogen, which can then be used for the reduction (Grünstein, B.P. 147118).

Durrans (J.S.C.I. 1935, **54**, 585) has discussed the process from the practical point of view, and proposals have been made to shorten it by passing the aldol with hydrogen under high pressure over a composite catalyst of nickel chromate which effects the simultaneous dehydration of the aldol and hydrogenation of the crotonaldehyde formed (Durrans, *l.c.*).

As carried out in the large plant of Industrial Solvents, Ltd., at Salt End, near Hull, alcohol vapour and air are passed over a silver gauze catalyst the temperature of which is maintained by the heat of reaction ; the hydrogen evolved is collected and stored for use in the subsequent process. The resultant acetaldehyde is condensed to acetaldol by means of aqueous caustic soda. The aldol is converted by steam distillation to crotonaldehyde, which is vaporised, mixed with the by-product hydrogen, and passed over a special catalyst. In 1930 the plant had a capacity of 1,500 tons of *n*-butyl alcohol per annum (*cf.* Chemical Age, Sept. 27, 1930).

(*d*) *Ethyl acetate.*—An interesting and technically important process for the manufacture of ethyl acetate consists in treating acetaldehyde with aluminium ethoxide. Tischtschenko, the discoverer of this curious reaction, recommended the following method of working (J. Russ. Phys. Chem. Soc. 1906, **38**, 398–418 ; Chem. Zentr. 1906, ii, 1309, 1552) :—acetaldehyde is cooled to −20°C., coarse aluminium ethoxide is added, and the mixture allowed to stand for some days, after which the ethyl acetate formed is distilled off. The maximum yield, 69·1%, was obtained using 15% of aluminium ethoxide ; using smaller amounts of catalyst the yield became progressively less with increased formation of by-products, and with 4·0% or less catalyst the formation of by-products predominated.

The process may be greatly improved by the addition of a promoter such as tin chloroethyoxide; for example 150 parts of acetaldehyde are cooled to 0°C., and a mixture of 9 parts aluminium ethoxide previously fused with 10% of its weight of tin chloroethoxide is added, during half an hour, with vigorous stirring and efficient cooling. (The requisite tin chloroethoxide is prepared from 20 parts stannic chloride and 14 parts absolute alcohol.) After about 10 hours the odour of acetaldehyde has disappeared ; the product is then distilled, giving a 96% yield of almost pure ethyl acetate boiling between 74° and 80°C. (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 26825, 1913).

A comparative experiment omitting the tin chloroethoxide gave only a 19% yield.

In B.P. 26826, 1913, by the same firm, a further improvement is claimed in which anhydrous aluminium ethoxide is replaced by the same substance previously treated with a small quantity of water, or a substance containing the elements of water, such as aluminium hydroxide ; the following figures illustrate the improvement in yield :

State of Ethoxide	Al, per cent.	Yield of Ester, per cent.
Untreated . . .	17·7	21–23
Fused with a little water .	21·0	87
Fused with $Al(OH)_3$.	24·8	85

Further improvements are claimed in B.P. 4887, 1915, consisting in increasing the activity of the catalyst by dissolving suitable substances such as dehydrated potash alum, dehydrated copper sulphate, or camphor in the molten ethoxide, or by supercooling it, *e.g.* by melting aluminium ethoxide and cooling rapidly by pouring into a solvent or on to a metal plate ; ethyl acetate is a specially suitable solvent for the catalysts which may be employed either hot or cold. The use of aluminium ethoxide dissolved in a suitable organic solvent such as dry solvent naphtha is claimed in B.P. 1288, 1915 (Meister, Lucius, and Brüning).

British Industrial Solvents, Ltd., recommend the use of aluminium butoxide as a catalyst, in absence of aluminium chloride, some butyl acetate being formed as well (B.P. 362458), whilst the Carbide and Carbon Chemicals Corp. claim the use of an aluminium compound of glycol (aluminium ethylene glycoloxide monoethyl ether) for effecting the conversion (U.S.P. 1630593), and Wacker and Consort. f. Elektrochem. Ind. G.m.b.H. describe the production of an improved catalyst by the addition of zinc chloride to a solution or suspension of aluminium ethoxide in alcohol (B.P. 387621).

The preparation of the requisite aluminium ethoxide, which is now a commercial product (*cf.* Chem. Trade J. **89**, 410), is described in G.P. 286596, 293613, and 289157, according to which it may be obtained in good yield from aluminium and absolute alcohol by the addition of small amounts of mercuric chloride (in presence or absence of iodine or of halogen alkyls) ; ethyl alcohol may be replaced by other alcohols to yield the corresponding alkoxides (Meister, Lucius, and Brüning). The crude product is purified by vacuum distillation, the pure aluminium ethoxide distilling over readily and solidifying to a snow-white mass ; it may also be distilled under normal pressure with suitable precautions, *e.g.* by the use of a shallow type of distilling vessel. The Chem. Fabr. auf Actien (vorm. E. Schering) recommends the gradual addition of ethyl alcohol containing iodine, mercuric chloride or stannic chloride to an excess of finely divided aluminium, suspended in molten aluminium ethoxide or in toluene or xylene (B.P. 245473). The same patentee also describes the preparation and use of complex metal alkoxides such as (**Mg**+**Al**), (**Na**+**Al**), etc., by treating metal alloys with alcohol, or by mixing the alkoxides in a neutral solvent (B.P. 261377).

Kagan and Sobolev have investigated the conversion of acetaldehyde to ethyl acetate by means of aluminium ethoxide and butoxide. Yields of 80% of ester were obtained when aluminium chloride was also present, as against 50% without the addition. For the production of 1 kg. of ester 2 g. of aluminium chloride and the alkoxide equivalent to 7 g. of aluminium were required (J. Chem. Ind. Russ. **1933**, **2**, 35 ; A. 1933, 806).

An alternative method for the preparation of ethyl acetate is given by Soc. Anon. des Aciéries et Forges de Firminy, consisting in the electrolytic oxidation of paraldehyde in 10% sulphuric acid containing salts of manganese, cerium, molybdenum, or vanadium, with subsequent addition of ethyl alcohol (B.P. 124195, 131600).

(*e*) *Aldehyde resins.*—A number of methods have been patented for the production of resinous or plastic substances from acetaldehyde which may be referred to shortly here : gaseous acetaldehyde when led into a mixture of phenol and a strong acid in presence of mercury salts yields transparent resins (G.P. 422904) ; or acetaldehyde and phenol may be condensed together by means of hexamethylene tetramine (Baekeland and Gotthilf, U.S.P. 1598546) ; the resultant resins may be further hardened by the addition of furfural or furfuramide (Alexander and Stokes, B.P. 243470). The preparation of synthetic resins from phenol and aldehyde forms the subject of B.P. 360380–1 and 360393 (void) (British Thomson-Houston Co., Ltd.). Synthetic resins may also be obtained without the use of phenol by subjecting aldehyde or crotonaldehyde to the prolonged action of an acid (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 187619), or from acetaldehyde, acetone, and glyceryl abietate, etc. (Varnol Chemical Corporation, B.P. 315870). Infusible resins are obtained from furfural and acetaldehyde (Kappeler, B.P. 345891), whilst formaldehyde when condensed with acetaldehyde and aldol, etc., either separately or together, produces water-soluble condensation products (I.G. Farbenind. A.-G., B.P. 349556).

The purification of such products is dealt with in the following patents : Hermann and Deutsch purify the resins by a process of solution and precipitation (U.S.P. 1596971), or the condensation product may be stabilised towards water by solution in acetic acid and precipitation in powder form by water (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 182459), or by grinding up with dilute acid (*idem*, B.P. 184442) ; the products may be improved by melting with ricinoleic acid, castor oil, salicylic acid, etc. (*idem*, B.P. 201916), or the softening points may be raised by treatment with alumina (*idem*, B.P. 394946).

According to B.P. 189190 (Badische Anilin- u. Soda-Fabrik) synthetic tanning agents may be prepared from phenolic substances and aldol, or from the condensation products of acetaldehyde and formaldehyde, in presence of waste sulphite liquor.

This subject will be more fully treated in article PLASTICS. *See also* “ Chemistry of Synthetic Resins,” Ellis (New York, 1935).

(vi) CONDENSATION PRODUCTS WITH AMINES. —A considerable number of investigations have dealt with condensation products of acetaldehyde with a variety of amino compounds. The preparation of water-soluble condensation products from amines or amides and acetaldehyde disulphonic acid to form substances of the general formula $RN:CH{\cdot}CH(SO_3H)_2$ (where $R=$ alkyl aryl or acyl radicals) is described in G.P. 448738. The products in this case are readily hydrolysed, regenerating the base. The chrysoidine compound can be utilised as a dyestuff of the “ Ionamine ” type for dyeing acetate silk (Mariam, Buttinschön, and I.G. Farbenind. A.-G.).

In most cases, however, the products are intended for use in the rubber industry either as *vulcanisation accelerators* or as *anti-agers*, of which the following examples may be noted : acetaldehyde is condensed with primary or secondary amines or amides, such as mono- or diethylamine, hydroxylamine, urea, phenyl hydrazine, *m*-nitraniline (Naugatuck Chemical Co., B.P. 180978) ; this process is modified in B.P. 216478 and 220320 by mixing rather more than 2 mols. acetaldehyde with 1 mol. aniline, in presence of an aqueous solution of $p_{\rm H}=3$ to 9, *e.g.* dilute acetic acid buffered with sodium acetate, at 40°–50°C. (Cadwell and Naugatuck Chemical Co.). The same inventors, in B.P. 240407, claim the production of *deterioration retarders* by condensing equimolecular proportions of aldehyde and aromatic amines, whilst in B.P. 279815 and 298537 the condensation products from aldehyde and amines are halogenated to form vulcanisation accelerators. Du Pont de Nemours & Co. prepare vulcanising catalysts by condensing acetaldehyde with aniline at 70°–85°, adding formaldehyde, and raising the temperature to 85°–125°C. Acetaldehyde and acetylene are passed into an amino such as *p*-aminophenol or *p*-aminodimethylaniline to produce accelerators (Rubber Service Laboratories, Ltd., B.P. 269556), or crotonaldehyde may be condensed with an aromatic amine to produce a brittle resinous product (I.G. Farbenind. A.-G., B.P. 270433). A material conferring good ageing properties on rubber is obtained by condensing acetaldehyde with *a*- or *β*-naphthylamine in presence of an acid (Cronshaw, Naunton, and British Dyestuffs Corporation, Ltd., B.P. 280661). A similar claim is made by Robinson and the Clayton Aniline Co. in B.P. 316761, or by further heating the product with diethylamine below 100°C. (B.P. 317205). Similar claims are made by I.G. Farbenind. A.-G. in B.P. 333941.

The product of *anilino-butylideneaniline* from aniline and aldehyde in alcoholic solution forms the subject of B.P. 286288 (Sebrell and Goodyear Tyre and Rubber Co.) ; the same inventors claim the preparation of *anti-agers* for rubber by condensing crotonaldehyde with toluidines, xylidines, and naphthylamines in presence of dilute hydrochloric acid (B.P. 287445. *Cf. also* B.P. 363644, Rubber Service Laboratories, Ltd.), and also the production of an accelerator by causing to react together a mercaptothiazole and an acetaldehyde-amine condensation product (*e.g.* from aniline and acetaldehyde, or crotonaldehyde) (B.P. 287051). Red resinous products soluble in dilute acids are obtained by condensing primary aromatic amines such as aniline with acetylene in the presence of mercury salts (Society of Chemical Industry in Bâle, B.P. 292168). According to Neale, Thomas, and the Dunlop Rubber Co., Ltd., a rubber anti-oxidant may be obtained by condensing aldol or crotonaldehyde with *p*-aminophenol (B.P. 311930). Vulcanising accelerators may also be obtained by allowing acetaldehyde or crotonaldehyde to react with sodium *a*-anilinoethanesulphonate (Fritsche and Clayton Aniline Co., Ltd., B.P. 326525).

(vii) MISCELLANEOUS REACTIONS. — When

heated alone to a high temperature acetaldehyde is decomposed into carbon monoxide and methane (Bone and Smith, J.C.S. 1905, **87**, 910 ; Ipatieff, Chem. Zentr. 1906, ii, 87 ; Nef, Annalen, 1901, **318**, 198). Owing to the importance of the reaction $CH_3{\cdot}CHO \rightarrow CH_4 + CO$, in connection with theories of combustion, the thermal decomposition has been very fully investigated and the following papers may be referred to : Hinshelwood and Hutchison, Proc. Roy. Soc. 1926, A, **111**, 380 ; Hinshelwood and Fletcher, *ibid.* 1933, A, **141**, 41 ; Trans. Faraday Soc. 1934, **30**, 614 ; Hinshelwood, Fletcher, Verhoek, and Winkler, Proc. Roy. Soc. 1934, A, **146**, 327 ; Hinshelwood and Winkler, *ibid.* 1935, A, **149**, 355 ; Hinshelwood, Nature, 1935, **135**, 67 ; Letort, Compt. rend. 1933, **197**, 1042 ; 1934, **199**, 351, 1617 ; Bone, Chem. and Ind. 1934, **53**, 813 ; Travers, Nature, 1934, **134**, 569 ; Rice and Hertzfeld, J. Amer. Chem. Soc. 1934, **56**, 284 ; Allen and Sickmann, *ibid.* 1251, 2031 ; Fromherz, Z. physikal. Chem. 1934, B, **25**, 301 ; Ebert, J. Physical Chem. 1935, **39**, 421 ; Patat and Sachsse, Naturwiss. 1935, **23**, 247 ; Travers, Nature, 1935, **135**, 511. The mechanism of the chain photolysis of acetaldehyde is discussed by Leermakers in J. Amer. Chem. Soc. 1934, **56**, 1537. Action of silent electric discharge on acetaldehyde, *see* Besson and Fournier, Compt. rend. 1910, **150**, 1238. Action of ultraviolet rays, *see* Berthelot and Gaudechon, Compt. rend. 1913, **156**, 233.

The vapour of acetaldehyde or its solution in benzene or alcohol slowly hardens dry gelatine films (Beckmann, Chem. Zentr. 1896, ii, 930 ; G.P. 116446, 116800).

Synthetic rubber.—For a discussion of the possibilities of producing a synthetic rubber directly from acetaldehyde, *see* Dubosc, Caoutchouc et Gutta Percha, **9**, 6608, 6713. In the presence of alumina at 400°C., *iso*propyl alcohol condenses with acetaldehyde to give a good yield of piperylene (Ostromisslenski, J. Russ. Phys. Chem. Soc. 1915, **47**, 1507). By passing acetaldehyde and alcohol vapours over heated catalysts such as alumina, phosphoric acid, etc., butadiene is formed (*ibid.* **47**, 1494, 1509). Precipitated alumina is specially noted as a suitable catalyst. Electrolytic reduction of a mixture of acetone and acetaldehyde yields $\beta:\delta$-*pentandiol* which may be dehydrated to piperylene by means of phosphoric acid (Plauson and Vielle, B.P. 156145). Acetaldehyde condenses with methyl ethyl ketone to form γ-methyl-δ-hydroxy-β-pentanone,

$$CH_3{\cdot}CO{\cdot}CHMe{\cdot}CH(OH){\cdot}CH_3,$$

which, on catalytic reduction and subsequent dehydration, affords γ-methyl-$\Delta^{\beta\delta}$-pentadiene, $CHMe:CMe{\cdot}CH:CH_2$, which, however, unlike butadiene or isoprene, does not polymerise to rubber-like masses (Fisher and Chittenden, Ind. Eng. Chem. 1930, **22**, 869).

Two "omnibus" patents dealing with the synthesis of rubber from acetaldehyde may be noted here : B.P. 307808 (grant of patent refused) and B.P. 320362 (I.G. Farbenind. A.-G.).

When subjected to *electrolysis* in faintly alkaline or neutral solutions, acetaldehyde is converted into alcohol and acetic acid (Slaboszewicz, Chem. Zentr. 1903, i, 279 ; Law, J.C.S. 1905, 198 ; Jackson and Laurie, J.C.S. 1906, **89**, 156).

Formaldehyde is obtained on passing a mixture of acetaldehyde and air over heated catalysts such as copper, silver, gold, cadmium, lead, bismuth, iron, nickel, vanadium pentoxide, cerium dioxide, etc. (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 178842; G.P. 349915).

The action of *zinc chromite upon acetaldehyde* at 360°C., and 210 atm., leads to the formation of a complex mixture of saturated and unsaturated alcohols, aldehydes, and esters (Adkins, Folkers, and Kinsey, J. Amer. Chem. Soc. 1931, **53**, 2714, 4220), whilst the production of *n-butyl alcohol, caproic acid esters*, and high-boiling resins by a variety of metal oxide catalysts at 300°C., and 200 atm., has been examined by Kinsey and Adkins, the copper oxide-chromium oxide catalyst being the most active in the production of esters (Ind. Eng. Chem. 1933, **24**, 314; *cf.* B.P. 287846, Bond, Smith, Lazier, and Du Pont de Nemours & Co.).

The preparation of *ketols* is noted in B.P. 264830 (I.G. Farbenind. A.-G.) ; thus, acetone treated with powdered potassium hydroxide at 5°C. yields the potassium compound of diacetone alcohol in the presence of which acetone condenses with acetaldehyde to form *hydracetylacetone* ; in the same way crotonaldehyde and acetone yield a ketol dehydrating to crotylidene acetone ; acetaldehyde and acetophenone yield *ethylidene acetophenone*, whilst acetaldehyde and *cyclo*hexanone afford o-*ethylidene*-cyclo-*hexanone*, the various products being of value as perfumes (*cf. also* B.P. 390905, Langwell, Youell, and Brit. Industrial Solvents, Ltd.).

Acetaldehyde condenses with acetoacetic ester in presence of potassium carbonate at 0° to −15°C., to *ethyl di-α′-hydroxyethylacetoacetate*, m.p. 33°C., which is unstable and changes above 20°C. to *ethyl α′-hydroxyethylacetoacetate* (Gault and Wendling, Compt. rend. 1934, **199**, 1052). *Acetaldehyde trimethylene acetal*, b.p. 107°, *see* Leutner, Monatsh. 1932, **60**, 317.

Cyanoacetic acid condenses with acetaldehyde to form a *dimeride of crotononitrile*, b.p. 130°–132°C./14 mm., and *β-methyl-glutarimide*, m.p. 145°–147°C. (Heim, Bull. Soc. chim. Belg. 1932, **41**, 320).

3-*Methylal-pentane* and 3-*methylol-pentane* may be obtained by condensing acetaldehyde with butyraldehyde (Wacker, Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 405141).

Detection and Estimation.

Detection.—One of the most characteristic properties of acetaldehyde is the pleasant apple-like odour of the vapour when considerably diluted with air. In aqueous solution acetaldehyde very readily reduces an ammoniacal solution of silver nitrate, giving a bright metallic mirror. Acetaldehyde (like all aldehydes which are stable in aqueous soda solution) can be detected by adding to the suspected solution in dilute alkali a fresh solution of 1 part *para*-diazobenzene sulphonic acid in 60 parts of water, rendered just alkaline with a little soda, and then some sodium amalgam ; if an aldehyde is present a reddish-brown colour is developed after 10–20 minutes (Penzoldt and Fischer, Ber. 1883, **16**, 657). A solution of rosaniline which has been decolorised by sulphurous acid, or of magenta bleached by sunlight, develops a violet colour on addition of acetaldehyde (or other aldehyde) (Villiers and Foyolle, Compt. rend. 1894, **119**, 751 ; Blaser, Chem. Zentr. 1899, ii, 848 ; Denigès, Compt. rend. 1910, **150**, 529), the reaction being due to the formation of the coloured compound

$$HN : C_6H_4 : C(C_6H_4{\cdot}NH{\cdot}SO{\cdot}O{\cdot}CHMe{\cdot}OH)_2$$

by the condensation of the aldehyde and magenta (Urbain, Bull. Soc. chim. 1896, iii, **15**, 455 ; Wieland and Scheuing, Ber. 1921, **54** [B], 2527) ("Schiff's reaction," 1867).

With salts of *meta*-diamines aldehydes give coloured solutions with intense greenish fluorescence (Bittó, Z. anal. Chem. 1897, **36**, 369). With sodium nitroprusside and alkali, acetaldehyde gives a cherry-red coloration, whilst if trimethylamine be first added, a blue colour is produced ; (Bittó, Annalen, 1892, **267**, 372 ; 1892, **269**, 377 ; Denigès, Bull. Soc. chim. 1897 [iii], **17**, 381 ; Simon, Compt. rend. 1897, **125**, 1105 ; Bull. Soc. chim. 1898 [iii], **19**, 297).

An examination of the various qualitative tests for acetaldehyde shows the following limits of sensitivity, in parts per million :

Reagent.	Sensitivity.
Ammoniacal silver nitrate . .	1,000
Potassium hydroxide . . .	40
Diazobenzene sulphonic acid .	3
Schiff's reagent (+0·1% of pyrogallol)	2
Tollen's reagent. . . .	1
Nessler's reagent . . .	1

(Middleton and Hymas, Analyst, 1931, **56**, 238).

For the detection of acetaldehyde formed during fermentation processes Neuberg recommends that 3 c.c. of liquid be treated with 0·5 c.c. of 4% sodium nitroprusside solution, and 2% of a 3% piperidine solution ; the presence of acetaldehyde is indicated by a deep blue coloration (Woch. Brau. 1919, **36**, 392). Both formaldehyde and acetaldehyde give a white precipitate with Bial's reagent (orcinol, ferric chloride and hydrochloric acid), but may be distinguished by their behaviour on heating, or with alkali (Sumner, J. Amer. Chem. Soc. 1923, **45**, 2378) ; according to Griebel (Z. Nahr. Genussm. 1924, **47**, 438) the presence of 0·001 mg. of acetaldehyde in fruits can be detected by means of its *p*-nitrophenylhydrazone.

Other tests for aldehydes are described by Ihl, Chem.-Ztg. 1890, **14**, 1571 ; Doebner, Ber. 1894, **27**, 352, 2020 ; Lumière and Seyewetz, Bull. Soc. chim. 1898 [iii], **19**, 134 ; Rimini, Atti R. Accad. Lincei, 1901, **10**, 355 ; Astruc and Murco, Compt. rend. 1900, **131**, 943 ; Riegler, Frdl. **42**, 168 ; Behrens, Chem.-Ztg. 1902, **26**, 1125 ; Sadtler, J.S.C.I. 1904, **23**, 387; Prudhomme, Bull. Soc. Ind. Mulhouse, 1904, **74**, 169 ; Leys, J. Pharm. Chim. 1905, **22**, 107 ; Auld and Hantzsch, Ber, 1905, **38**, 2677.

For identification purposes the following crystalline derivatives may be noted :

Phenylhydrazone, α-form, m.p. 98°–101° ; β-form, m.p. 57° (Lockemann and Liesche, Annalen, 1905, **342**, 14 ; Laws and Sidgwick, J.C.S. 1911, **99**, 2085).

p-*Chlorophenylhydrazone*, m.p. 98°–99° (Sah, Lei, and Shen, A. 1933, 964).

p-*Nitrobenzenesulphonhydrazone*, m.p. 121°–122° (Cameron and Storrie, J.C.S. 1934, 1330).

2 : 4-*Dinitrophenylhydrazone*, m.p. 146° (Cameron and Storrie, *l.c.* ; Ingold, Pritchard, and Smith, J.C.S. 1934, 79 ; Bryant, J. Amer. Chem. Soc. 1933, **55**, 3201).

m-*Nitrobenzoylhydrazone*, m.p. 160–161° (Meng and Sah, A. 1934, 1376).

o-*Chlorobenzoylhydrazone*, m.p. 145° (Sun and Sah, A. 1934, 1376).

p-*Chlorobenzoylhydrazone*, m.p. 180°–181° (Shih and Sah, A. 1934, 1376).

Phenylsemicarbazone, m.p. 151°–152° (Sah and Ma, J. Chinese Chem. Soc. 1934, **2**, 32 ; A. 1934, 791).

p-*Tolylsemicarbazone*, m.p. 174°–175° (Sah and Lei, J. Chinese Chem. Soc. 1934, **2**, 167 ; A. 1934, 1016).

Thiosemicarbazone, m.p. 146° (Freund and Schander, Ber. 1902, **35**, 2602).

4 : 4′-*Diphenylsemicarbazone*, m.p. 133°–134° (Toschi and Angiolani, Gazzetta, 1915, **45**, i, 205).

Estimation.—Earlier references : Rieter, Chem. Zentr. 1896, ii, 368 ; Rocques, Compt. rend. 1898, **127**, 526, 764 ; Seyewetz and Bardin, Bull. Soc. chim. 1905 [iii], **33**, 1000 ; Colles, J.C.S. 1906, **89**, 1249 ; Soboleff and Zalewski, Z. physiol. Chem. 1910, **69**, 441.

Colorimetric methods have been devised by Paul (Z. anal. Chem. 1896, **35**, 649) ; Tolman (J. Amer. Chem. Soc. 1906, **28**, 1624). A further method based upon the yellow coloration produced with benzidine hydrochloride is described by Smith (Bull. Bio. Techn. 1922, No. 5, 117).

Neuberg (Biochem. Z. 1931, **232**, 479) recommends estimation of acetaldehyde by means of the 2 : 4-dinitrophenylhydrazone, a method which has also been investigated by Iddles and Jackson (Ind. Eng. Chem. [Anal. Edn.], 1934, **6**, 454).

In presence of ethyl alcohol Pelgrom (Natuurwetensch. Tijds. 1932, **14**, 44 ; A. 1932, 632) recommends the addition of mercuric oxide to one half of the aqueous solution, the alcohol being then distilled off and determined by the bichromate method, whilst in the remaining half of the solution the total acetaldehyde plus alcohol is determined by titration with bichromate and the aldehyde estimated by difference. Alternatively the aldehyde may be converted into the bisulphite compound, which, after removal of the alcohol, is decomposed again and the $KHSO_3$ estimated with iodine solution.

The estimation in admixture with ethyl alcohol and acetone by preferential oxidation with chromic acid is detailed by Hoepner (Z. Nahr. Genussm. 1917, **34**, 453).

Stipp and Fricke estimate acetaldehyde by treating its aqueous solution with an excess of alkaline ammoniacal silver nitrate solution, and then titrating the reduced silver with ammonium thiocyanate (Z. physiol. Chem. 1921, **116**, 293).

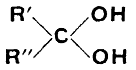
Hagglund has examined the estimation of acetaldehyde in presence of acetone (Z. anal. Chem. 1914, **53**, 433), as also has Yamada (J. Soc. Chem. Ind. Japan, 1933, **36**, 193 ; A. 1933, 937), who determines the aldehyde by oxidation with silver oxide, the acetone being estimated by difference, after titration of total aldehyde and acetone by means of sodium bisulphite and iodine.

Platonov and Plakidina (J. Gen. Chem. Russ. 1934, **4**, 472 ; A. 1934, 1376) describe a method for estimating a mixture of acetone, acetaldehyde, and acetic acid : the acid is titrated with barium hydroxide solution, the combined acetone and acetaldehyde is found by adding hydroxylamine hydrochloride and titrating the liberated hydrochloric acid, and the acetone is finally estimated iodometrically, after oxidising the aldehyde by means of potassium permanganate.

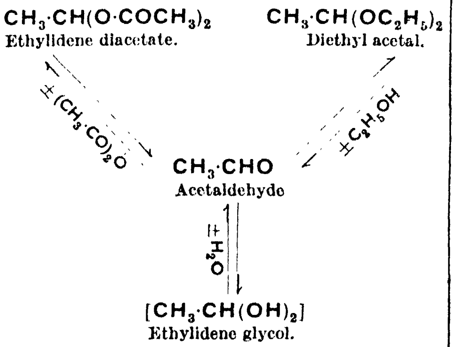
For the estimation of acetaldehyde in presence of paraldehyde, *see* Richter (Pharm. Ztg. 1912, **57**, 125) ; Heyl (*ibid.* 1883, **28**, 165, 720).

F. A. M.

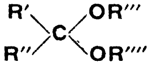
ACETALS. The systematic nomenclature is : 1 : 1-dialkyloxyalkane (Smith, J.C.S. 1936, 1072). The term is applied to the esters and ethers of the so-called *gem*-glycols of the type :



(where R′ and R″ may be either hydrogen or an aliphatic or aromatic radical) which are themselves, in general, incapable of existence, as they immediately lose a molecule of water with formation of the corresponding aldehyde or ketone. Thus, in the case of ordinary acetaldehyde we have the relationships :



Acetals therefore possess the general formula



where R′ and R″ may be alkyl or aryl radicals or hydrogen, and R‴, R⁗ are acidyl, alkyl, or aralkyl radicals. Two types of acetals may be distinguished according to whether the products are alkyl ethers or acid esters. The term *acetal* is more usually applied to the ethers, but owing to the close analogy between the two classes it is convenient to include the esters of *gem*-glycols in the same group.

I. Dialkyl Ethers of *gem*-Glycols

(Acetals of Aldehydes and Ketones).

METHODS OF PREPARATION.—On mixing an aldehyde (*e.g.* acetaldehyde) and ethyl alcohol no reaction occurs at first, but on standing heat is evolved due to the formation of a *hemi-acetal* :

$$CH_3{\cdot}CHO + EtOH \rightleftharpoons CH_3{\cdot}CH(OEt)(OH)$$

(Adkins and Broderick, J. Amer. Chem. Soc. 1928, **50**, 499). On heating the mixture a certain amount of diethyl acetal is produced by further reaction between the hemi-acetal and a second molecule of alcohol but the yield is poor :

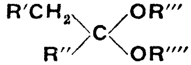
$$CH_3{\cdot}CH(OEt)(OH) + EtOH \rightleftharpoons CH_3{\cdot}CH(OEt_2) + H_2O$$

(Geuther, Annalen, 1863, **126**, 62). The yield is improved by the addition of a small quantity of a catalyst such as a mineral acid or ferric chloride to the mixture of alcohol and aldehyde (Trillat and Cambier, Compt. rend. 1894, **118**, 1277), but the standard method for many years was that of Fischer and Giebe (Ber. 1897, **30**, 3053 ; 1898, **31**, 545), which consisted in passing about 1% (by weight) of hydrogen chloride into the mixture, heating, and allowing to stand for some time. After removal of the acid by means of potassium carbonate the product was fractionally distilled, the yield of acetal being about 50%. Haworth and Lapworth (J.C.S. 1922, **121**, 76) have shown that the yield of acetals by Fischer and Giebe's method is increased if the hydrochloric acid be neutralised before extraction of the acetal, by the addition of sodium ethoxide. In this way the yield, for instance, of benzaldehyde diethyl acetal is increased from 36 to 80%. In an alternative method Haworth and Lapworth heated together benzaldehyde, alcoholic hydrochloric acid and benzene, collected the ternary distillate consisting of water, alcohol, and benzene in a flask containing calcium carbide heated to 120°C., returning the dried residual vapours to the original flask ; the yield of benzaldehyde diethyl acetal in this case was 66%. A yield of 74% was obtained on substituting the hydrochloric acid by a 0·6% alcoholic solution of ammonium chloride.

Bedowé (Bull. Soc. chim. Belg. 1925, **34**, 41) states that acetals may be prepared by heating an alcohol with paraldehyde and 1–2% of toluene-*p*-sulphonic acid, the resultant acetal being separated by the addition of carbon disulphide ; the Société anon. des Distilleries des Deux Sèvres claim (B.P. 283112) that in the catalytic production of an acetal from acetaldehyde and an alcohol, the mixture, after reaction, is distilled to remove the unchanged aldehyde and part of the alcohol and finally after addition of benzene the water and remainder of the alcohol are distilled off in the form of an azeotropic mixture (*cf.* Haworth and Lapworth, *supra*).

An important industrial method for the production of acetals of acetaldehyde consists in passing a stream of acetylene into an alcohol in presence of a suitable catalyst, usually a mercury salt; this is described under the heading of diethyl acetal. The general problem of the production of acetals from acetylene is discussed by Reichert, Bailey, and Nieuwland (J. Amer. Chem. Soc. 1923, **45**, 1552). All the acetals of the monohydric alcohols from methanol to nonyl alcohol were prepared from acetylene and the alcohol by Hinton and Nieuwland (J. Amer. Chem. Soc. 1930, **52**, 2892), using as a catalyst a solution of boron fluoride in methyl alcohol together with mercuric oxide.

A less general method for the production of acetals of the type



$$R'CH_2(R'')C(OR''')(OR'''')$$

by combining vinyl ethers, $CHR' : CR''\cdot OR'''$, with organic hydroxy compounds, is claimed by the I.G. Farbenind. A.-G. in B.P. 352474 (*cf. also* B.P. 352070).

A convenient general method for the preparation of the simpler acetals is that of King and Mason (B.P. 101428), which consists in treating a mixture of the aldehyde and alcohol with certain metallic salts (or their saturated aqueous solutions) such as the chlorides or nitrates of aluminium, calcium, cerium, magnesium, manganese, etc., preferably in presence of a small quantity of mineral acid: thus, acetaldehyde (50 g.) and 95% alcohol (120 g.) are mixed and anhydrous calcium chloride (20 g.) is added; the mixture becomes warm and finally separates into two layers, the upper of which is removed, washed and dried successively over calcium chloride and potassium carbonate. On distillation it yields 120 g. acetal, or 90% of theory. According to Adkins and his co-workers the catalytic effect of salts in promoting acetal formation is connected with their tendency to form alcoholates (Adams and Adkins, J. Amer. Chem. Soc. 1925, **47**, 1358, 1368; Pfeiffer and Adkins, *ibid.* 1931, **53**, 1043, 1051; Adkins and Conner, *ibid.*, **53**, 1091; Adkins, Folkers, and Kinsey, *ibid.* **53**, 2718).

Another general method for the production of acetals consists in heating an acetal with an excess of an alcohol, when partial interchange of the alcohol groups takes place:

$$RCH(OR')_2+2R''OH \rightleftharpoons RCH(OR'')_2+2R'OH$$

In this way diethyl acetal on heating with excess of methyl alcohol is converted almost completely into dimethyl acetal. In general, the acetal series may be descended by heating any member of the group with an alcohol containing a lesser number of carbon atoms, but in presence of a little hydrochloric acid an equilibrium mixture is obtained containing all possible products, those of higher molecular weight predominating (Delépine, Compt. rend. 1901, **132**, 331, 968; Bachmann, Annalen, 1883, **218**, 44).

An important general laboratory method is that of Claisen (Ber. 1896, **29**, 1007; 1898, **31**, 1010; 1907, **40**, 3903), consisting in treating an aldehyde or ketone with orthoformic ester in alcoholic solution in presence of a suitable catalyst, such as a mineral acid, oxalic acid, ammonium chloride, sulphate or nitrate, etc. (*cf. also* Arbusow, Ber. 1907, **40**, 3301; Claisen, *ibid.* 3912). Helferich and Hausen (Ber. 1924, **57** [B], 795) claim that orthosilicic esters can advantageously replace orthoformic esters as a reagent in the direct preparation of acetals, and Voss (Annalen, 1931, **485**, 258, 283) similarly employs alkylsulphites. Again, orthoformic esters can also react with alkyl magnesium salts to yield acetals (Bodroux, Compt. rend. 1904, **138**, 700; Tschitschibabin, Ber. 1904, **37**, 186), or with halogenated fatty esters in presence of zinc (Tschitschibabin, J. pr. Chem. 1905 [2], **72**, 326; Claisen, Ber. 1898, **31**, 1019):

$$CH(OEt)_3+CHMeBr\cdot COOR+Zn \rightarrow CH(OEt)_2\cdot CHMe\cdot COOR+ZnBr(OEt)$$

$$CH(OEt)_2\cdot CHMe\cdot COOR \rightarrow CH(OEt)_2\cdot CHMe\cdot COOH \rightarrow CH(OEt)_2\cdot CH_2Me$$

Certain special methods for the preparation of methylformal (the acetal derived from formaldehyde) are available and are described in connection with that substance.

Mixed acetals containing two different alcohol residues have been described by Bachmann (*l.c.*), but according to Rübencamp (Annalen, 1884, **225**, 271) and Fritz and Schumacher (Annalen, 1894, **279**, 308) these consist of mixtures of two acetals in molecular proportions. Delépine, however (Compt. rend. 1901, **132**, 331, 968), claims to have obtained mixed acetals.

Cyclic acetals, of use in perfumery and as industrial solvents, are made by condensing dihydric alcohols with unsubstituted araliphatic aldehydes (B.P. 346115, I.G. Farbenind. A.-G.; G.P. 419223, Farbw. vorm. Meister, Lucius, u. Brüning).

GENERAL PROPERTIES.—The true acetals, or dialkyl ethers of *gem*-glycols, are colourless liquids of pleasant ethereal odour which can be distilled without decomposition. The lower members are slightly soluble in water, by which they are slowly hydrolysed, but on boiling or on the addition of a little mineral acid they are hydrolysed with great rapidity; in most cases they are stable to dilute alkalis, even on boiling. They can be separated from their aqueous solutions by the addition of calcium chloride, and are miscible with alcohol and ether.

The acetals can form double compounds with various metallic salts such as magnesium or zinc iodides, calcium chloride and magnesium bromide, *e.g.* $2CH_2(OCH_3)_2,MgBr_2$, m.p. 112°; $2CH_3\cdot CH(OC_2H_5)_2,MgI_2$, m.p. 86° (Blaise, Compt. rend. 1905, **139**, 1211; 1906, **140**, 661; Menschutkin, Z. anorg. Chem. 1907, **53**, 31). Ethylformal forms a hydrate,

$$CH_2(OC_2H_5)_2,H_2O,$$

b.p. 74°–75°, which possesses an odour of rum and is slightly soluble in water; the higher homologues also form monohydrates boiling at lower temperatures than the acetals themselves (Trillat and Cambier, Compt. rend. 1894, **118**, 1278).

The acetals are of considerable use in replacing the free aldehydes or ketones in synthetic operations owing to their higher boiling-points (*e.g.* acetaldehyde, b.p. 20°; diethyl acetal, b.p. 104°), and also to the fact that alcohol and not water is split off during condensation reaction (*cf.* yield of vinyldiacetonamine from diacetonamine by use of acetal, King, Mason, and Schryver, B.P. 101738).

The acetals can be readily halogenated and converted into amino-, hydroxy-, alkoxy-, etc., derivatives which are useful synthetic reagents.

By leading the vapour of an acetal over a noble metal catalyst at 200°–350° unsaturated ethers are obtained (B.P. 345253, I.G. Farbenind. A.-G.), ethylacetal for example yielding vinyl ethyl ether.

FORMALS, $CH_2(OR)_2$.

Formals can be prepared from trioxymethylene by direct distillation with methyl, ethyl, *n*-propyl, *n*-butyl, *iso*butyl, and *n*-amyl alcohols in the presence of a non-volatile catalyst (Ghysels, Bull. Soc. chim. Belg. 1924, **33**, 57).

Methylal, $CH_2(OCH_3)_2$, or methylformal, b.p. 42·3°, d_4^0 0·885, can be obtained (i) by treating a mixture of methyl alcohol and 40% formalin solution with solid calcium chloride and a little hydrochloric acid (Fischer and Giebe, Ber. 1897, **30**, 3054); (ii) by treating methylene chloride with sodium methoxide (Arnhold, Annalen, 1887, **240**, 197); (iii) by treating a chloromethyl alkyl ether, $CH_2(OR)Cl$, with sodium methoxide (Favre, Compt. rend. 1894, **119**, 284; Bull. Soc. chim. 1894 [3], 11, 879; Henry, Ber. 1893, **26**, Ref. 933; Compt. rend. 1894, **119**, 425; de Sonay, Ber. 1894, **27**, Ref. 337); (iv) by heating polyoxymethylene and the required alcohol with 1–4% ferric chloride for some hours (Trillat and Cambier, Compt. rend. 1894, **118**, 1277).

It is a good solvent for many organic compounds and may be used for various condensations in place of formaldehyde.

The following formals are known but the higher members are of little importance:

Ethylformal, $CH_2(OC_2H_5)_2$, b.p. 87°; d^{20} 0·834 (Arnhold, *l.c.*; Greene, Chem. News, 1884, **50**, 75; Pratesi, Ber. 1883, **16**, 1870; Favre, *l.c.*; Trillat and Cambier, *l.c.*).

n-*Propylformal*, $CH_2(OC_3H_7)_2$, b.p. 137°; d^{20} 0·831 (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*; Favre, Bull. Soc. chim. 1894 [3], **11**, 881).

iso*Propylformal*, $CH_2(OC_3H_7)_2$, b.p. 118°; d^{20} 0·831 (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

iso*Butylformal*, $CH_2(OC_4H_9)_2$, b.p. 164°; d^{20} 0·825 (Arnhold, *l.c.*; Gorbow and Kessler, Ber. 1887, **20**, Ref. 778; Trillat and Cambier, *l.c.*).

iso*Amylformal*, $CH_2(OC_5H_{11})_2$, b.p. 207°; d^{20} 0·835 (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

Hexylformal, $CH_2(OC_6H_{13})_2+H_2O$, b.p. 174°–175°; d^{15} 0·822 (Trillat and Cambier, *l.c.*).

Octylformal, $CH_2(OC_8H_{17})_2$, b.p. 289°; d^{15} 0·848 (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

cyclo*Hexylformal*, $CH_2(C_6H_{11}O)_2$ (Murat and Cathala, J. Pharm. Chim. **6**, 289).

For the preparation of the simpler mixed formals, *see* Palomaa and Kantola (Ber. 1932, **65** [B], 1593).

ACETALS, $CH_3{\cdot}CH(OR)_2$.

Methylacetal, $CH_3{\cdot}CH(OCH_3)_2$, b.p. 64°–65°; d_4^{26} 0·849 (22°), occurs in crude wood spirit (Dancer, Annalen, 1864, **132**, 240; Alsberg, Jahresb. f. Chem. 1864, 485; Geuther and Bachmann, Annalen, 1883, **218**, 44; Schiff, Annalen, 1883, **220**, 104; 1884, **223**, 74; Hinton and Nieuwland, *l.c.*).

Ethylacetal, $CH_3{\cdot}CH(OC_2H_5)_2$ (ethylidene diethyl ether; ethane-diol (1 : 1)-diethyl ether), generally known simply as "acetal" (*cf.* Döbereiner, Gm., **4**, 805; Liebig, Annalen, **5**, 25; **14**, 156; Stas, Ann. Chim. Phys. [3], **19**, Wurtz, Ann. Chim. Phys. 1893 [3], **48**, 70; Geuther, Annalen, 1863, **126**, 63). The original method of Wurtz (*l.c.*) for the preparation of acetal by partial oxidation of ethyl alcohol with manganese dioxide and sulphuric acid and subsequent treatment of the reaction product is now merely of historic interest, as also are the methods of Geuther (*l.c.*) from alcohol and acetaldehyde in presence of acetic acid; of Wurtz and Frapolli (Compt. rend, 1868, **67**, 418; Annalen, 1858, **108**, 223) from monochlorethyl ether and sodium ethoxide; or the method of Engel and Girard (Compt. rend. 1881, **92**, 692; J. 1880, 694) from alcohol and acetaldehyde in presence of hydrogen phosphide.

The most practical and convenient method for the production of acetal is that of King and Mason (B.P. 101428, *vide supra*) (*see also* "Organic Syntheses," 1932, p. 1).

On a technical scale considerable interest attaches to the production of ethylacetal from acetylene and ethyl alcohol in presence of a mercury catalyst, by a modification of Kutscherow's acetaldehyde synthesis (*cf.* Kutscherow, Ber. 1881, **14**, 1540; 1909, **42**, 2759):

$$CH{\vdots}CH+2C_2H_5{\cdot}OH = CH_3{\cdot}CH(OC_2H_5)_2$$

The general method for the production of "ethers of ethylidene glycol" by the action of acetylene upon alcohols in presence of mercury salts was described by the Chemische Fabrik Griesheim Elektron in 1913 (B.P. 14246) (*see also* Boiteau, B.P. 15806, 1914), and a modification consisting in forming the catalyst *in situ*, *e.g.* by adding mercuric oxide or the mercury salt of a weak acid to the mixture, followed by sulphuric acid, was the subject of a later claim (B.P. 15919, 1914).

The Consortium f. Elektrochemische Industrie describe a general method for the production of acetals consisting in passing acetylene, mixed with the vapours of an alcohol, over heated catalysts such as the oxides or salts of cadmium, zinc, mercury, barium, calcium, silver, etc. (B.P. 182112), whilst later patents (B.P. 257622, 264791) claim the production of acetal from acetylene and alcohol in a continuous process, the product being removed as it is formed (to prevent resin formation) by the use of an immiscible solvent such as paraffin oil, or by carrying out the reaction under reduced pressure in a current of inert gas, or by the use of a salting-out agent such as potassium acetate. In all cases the alcohol used should contain a few per cent. of water.

Ethylacetal is a colourless liquid of agreeable fruity odour, b.p. 104°–105°, d_4^{20} 0·8314 (Brühl, Annalen, 1880, **208**, 25). It is soluble in 18 vols. of water at 25°, and is miscible with alcohol and ether in all proportions. It does not reduce ammoniacal silver solution and remains unaltered on exposure to air; it is, however, oxidised to acetaldehyde and acetic acid by platinum black. It is stable to alkalis but is very rapidly hydrolysed by dilute mineral acids to acetaldehyde and ethyl alcohol. (For formation and hydrolysis, *see* Lapworth and Fitzgerald, Proc. Chem. Soc. **24**, 153).

Acetal has some solvent power for cellulose esters (B.P. 14246, 1913). A use for acetal is suggested by Ostromisslenski (J. Russ. Phys. Chem. Soc. 1916, **47**, 1472, 1509), which consists in passing the vapour over a heated alumina catalyst at 360°–460° to produce butadiene for the manufacture of synthetic rubber (*cf. also* Boiteau, B.P. 15806, 1914). Its use in the production of a synthetic alkaloid *coralydine* (from tetrahydropapaverine and acetal) is described by Pictet and Malinowski (Ber. 1913, **46**, 2688 ; B.P. 17578, 1914).

Ethylacetal is converted by treating with phosphorus pentoxide into *vinyl ethyl ether*, a colourless liquid, b.p. 35·5°, $d^{14\cdot5}$ 0·762 :

$$\mathrm{CH_3{\cdot}CH(OC_2H_5)_2 - C_2H_5{\cdot}OH = CH_2 : CH{\cdot}O{\cdot}C_2H_5}$$

(Claisen, Ber. 1898, **31**, 1021). When heated with acetic anhydride at 150° one ethyl group is replaced by an acetyl group, yielding "acetaldehyde-ethyl acetate,"

$$\mathrm{CH_3{\cdot}CH(O{\cdot}C_2H_5)(O{\cdot}COCH_3)},$$

b.p. 125°–130°, *d* 0·941, which is hydrolysed by boiling water to acetaldehyde, ethyl alcohol, and acetic acid (Claisen, Ber. 1898, **31**, 1018).

Acetal does not give the iodoform reaction until shaken with a few drops of hydrochloric acid to hydrolyse it. Acetal may be estimated in presence of paraldehyde by the method of Orton and McKie (J.C.S. 1916, **109**, 184) by preferential hydrolysis of the acetal and determination of the acetaldehyde produced by the methods of Ripper (Monatsh. 1900, **21**, 1079) or Seyewetz (Bull. Soc. chim. 1905 [iii], **33**, 1000) (*cf. also* Feinberg, Amer. Chem. J. 1913, **49**, 97).

Derivatives of Ethylacetal.—Direct chlorination of acetal yields a mixture of di- and trichloracetal (Pinner, Ber. 1872, **5**, 148), which are also formed as intermediate products in the preparation of chloral (*q.v.*) from alcohol (*cf.* Lieben, Ann. Chim. Phys. 1894 [3], **52**, 313 ; Paternò, Compt. rend. 1868, **67**, 765 ; Krey, Chem. Soc. Abstr. 1877, 295), the products being purified by fractional distillation. An improved method from alcohol is described by Fritsch (Annalen, 1894, **279**, 288) which consists in chlorinating well-cooled alcohol until the product has d^{25} 1·02–1·03. Half the original volume of alcohol is added and the mixture heated to 50°–60° for a few hours ; the free acid is removed by calcium carbonate, the oil being then washed with water, dried and fractionated.

Monochloracetal, $\mathrm{CH_2Cl{\cdot}CH(OC_2H_5)_2}$, is a colourless liquid, b.p. 155°, d^0 1·0418, d^{15} 1·026 (Klien, Chem. Soc. Abstr. 1877, 291), or b.p. 156°–158° (Autenrieth, Ber. 1891, **24**, 159) (*cf.* Lieben, Annalen, 1868, **146**, 193 ; Paternò, Mazzara, Ber. 1873, **6**, 1202 ; Natterer, Monatsh. 1882, **3**, **444** ; **5**, 497 ; Wislicenus, Annalen, 1878, **192**, 106 ; Frank, Annalen, 1880, **206**, 341 ; Fritsch, Annalen, 1894, **279**, 300). When heated with bleaching powder it yields di- and trichloracetal, chloroform, and a chlorinated aldehyde (Goldberg, J. pr. Chem. 1881 [2], **24**, 107).

Dichloracetal, $\mathrm{CHCl_2{\cdot}CH(OEt)_2}$, b.p. 183°–184°, d^{14} 1·1383 (Jacobson, Ber. 1871, **4**, 217 ; Pinner, Ber. 1872, **5**, 148 ; Annalen, 1875, **179**, 34 ; Krey, *l.c.* ; Paternò, Annalen, 1869, **149**, 372, **150**, 134) ; it condenses with hydrocarbons (HX) to form compounds of the type $\mathrm{CHX_2{\cdot}CHCl_2}$ (Fritsch, Annalen, 1894, **279**, 319 ; Buttenberg, *ibid.* 324).

Trichloracetal, $\mathrm{CCl_3{\cdot}CH(OEt)_2}$, b.p. 204·8°, *d* 1·2813, obtained by the action of chlorine on alcohol (Byasson, Bull. Soc. chim. 1879 [ii], **32**, 304 ; Wurtz and Frapolli, J. 1872, 438 ; Paternò and Pisati, J. 1872, 303 ; Lieben, Paternò, Krey, *l.c.*).

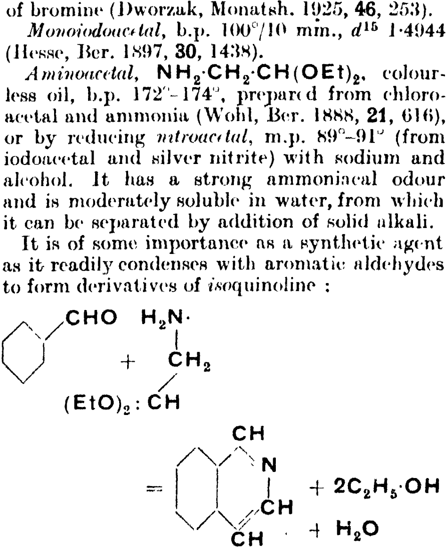
Monobromoacetal, b.p. 81°–82°/28 mm., prepared conveniently by brominating paraldehyde at 0°, mixing with absolute alcohol, standing for 12 hours, pouring the product into ice-cold aqueous potassium carbonate and, distilling the separated oil *in vacuo* (*cf.* Pinner, Ber. 1872, **5**, 149 ; Wislicenus, Annalen, 1878, **192**, 2551 ; Fischer and Landsleiner, Ber. 1892, **25**, 2551 ; Freundler and Ledru, Compt. rend. 1905, **140**, 794).

Dibromoacetal, $\mathrm{CHBr_2{\cdot}CH(OEt)_2}$, b.p. 96°–96·5°/10 mm., is prepared by the action of bromine (2 mols.) on paracetaldehyde below 0° ; an impure *tribromoacetal*, b.p. 120·5°–122·5°/10 mm. is similarly obtained by the action of 3 mols. of bromine (Dworzak, Monatsh. 1925, **46**, 253).

Monoiodoacetal, b.p. 100°/10 mm., d^{15} 1·4944 (Hesse, Ber. 1897, **30**, 1438).

Aminoacetal, $\mathrm{NH_2{\cdot}CH_2{\cdot}CH(OEt)_2}$, colourless oil, b.p. 172°–174°, prepared from chloroacetal and ammonia (Wohl, Ber. 1888, **21**, 616), or by reducing *nitroacetal*, m.p. 89°–91° (from iodoacetal and silver nitrite) with sodium and alcohol. It has a strong ammoniacal odour and is moderately soluble in water, from which it can be separated by addition of solid alkali.

It is of some importance as a synthetic agent as it readily condenses with aromatic aldehydes to form derivatives of *isoquinoline* :



Substituted alkylaminoacetals are also known (Paal and van Gember, Archiv. der Pharm. 1908,

246, 306 ; Störmer and Prall, Ber. 1897, **30**, 1504).

Acetal sulphide, $[(C_2H_5O)_2CH{\cdot}CH_2]_2S$, has been prepared by Fischer (Ber. 1909, **42**, 1070) by heating chloroacetal with aqueous potassium sulphide at 120°–150°C. Colourless liquid, b.p. 280°/750 mm. Readily soluble in water but can be salted out of solution.

Chlorotriethylphosphinoacetal, from monochloracetal and triethylphosphine, is a viscous liquid of overpowering odour, and hydrolyses to chlorotriethylphosphinoacetaldehyde. The *bromo*-compound is also described (Caldwell, J.C.S. 1916, **109**, 283).

HIGHER ALKYL ACETALS.—*Propylacetal*, $CH_3{\cdot}CH(O{\cdot}C_3H_7)_2$, b.p. 147°, d_4^{26} 0·825 (de Girard, Compt. rend. 1880, **91**, 629 ; Hinton and Nieuwland, J. Amer. Chem. Soc. 1930, **52**, 2893).

n-*Butylacetal*, $CH_3{\cdot}CH(O{\cdot}C_4H_9)_2$, b.p. 198°–200° (King and Mason, B.P. 101428), b.p. 197°–198°, d_0^{26} 0·831 (Hinton and Nieuwland, *l.c.*).

iso*Butylacetal*, $CH_3{\cdot}CH(O{\cdot}C_4H_9)_2$, b.p. 168°–169° ; d_4^{24} 0·812 (Claus and Trainer, Ber. 1886, **19**, 3006 ; de Girard, Compt. rend. 1880, **91**, 629 ; Hinton and Nieuwland (*l.c.*)).

iso*Amylacetal*, $CH_3{\cdot}CH(O{\cdot}C_5H_{11})_2$, b.p. 211°, d_4^{23} 0·828 (Alsberg, Jahresb. f. Chem. 1864, 485 ; Claus and Trainer, *l.c.* ; Hinton and Nieuwland, *l.c.*).

ACETALS OF HIGHER ALDEHYDES AND OF KETONES.—*Acrolein ethylacetal*,

$$CH_2{:}CH{\cdot}CH(OEt)_2,$$

b.p. 123·5°; d^{15} 0·8453, sparingly soluble in water (Wohl, Ber. 1898, **31**, 1796 ; for reactions, *see also* Wohl and Emmerich, Ber. 1900, **33**, 2761 ; Wohl and Schweitzer, Ber. 1907, **40**, 92).

β-Ethoxy-propaldehyde ethylacetal,

$$CH_2(OEt)CH_2{\cdot}CH(OEt)_2,$$

b.p. 184°–186°, is formed from acrolein and orthoformic ester (Claisen, Ber. 1897, **29**, 2933 ; 1898, **31**, 1014 ; Fischer and Giebe, Ber. 1897, **30**, 3056).

In a similar manner crotonaldehyde yields :

β-Ethoxybutaldehyde ethylacetal,

$$CHMe(OEt){\cdot}CH_2{\cdot}CH(OEt)_2,$$

b.p. 73°–74°/14 mm. (Claisen, *l.c.*).

Crotonaldehyde ethylacetal, *see* Wohl and Frank (Ber. 1902, **35**, 1904).

β-Chlorobutaldehyde ethylacetal is formed by saturating a mixture of crotonaldehyde and absolute alcohol with dry hydrogen chloride in the cold (Wohl and Frank, *l.c.*). It can be condensed with aniline to yield *β-anilinobutaldehyde ethylacetal*,

$$NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}CH(OEt)_2,$$

as a yellow viscous oil, b.p. 173°–175°/25 mm., 153°–154°/12 mm., which affords quinaldine on heating with phosphoric oxide (Mason, J.C.S. 1929, 1560).

Propiolaldehyde ethylacetal,

$$CH{:}C{\cdot}CH(OEt)_2,$$

formed from acrolein dibromide and alcoholic potassium hydroxide, is an oil, b.p. 140°, with a camphor-like odour (Claisen, Ber. 1896, **29**, 2933; 1898, **31**, 1015, 1022 ; 1903, **36**, 3664, 3668 ; 1907, **40**, 3907 ; Kendal and Ilford, Ltd., B.P. 390808). The use of this acetal and of *β-phenylpropiolaldehyde ethylacetal* (from monobromo-cinnamaldehyde diethylacetal) is noted in B.P. 390808 for the purpose of condensing with quaternary salts of heterocyclic nitrogenous bases, to produce dicarbocyanine dyes for photosensitisation of gelatine-silver emulsions.

An *acetal* for use as a plasticiser or solvent is prepared by heating glycol under pressure with 50% formaldehyde solution in presence of sulphuric acid (Dreyfus, B.P. 393608 ; *cf. also* Pinner, Ber. 1872, **5**, 150 ; Verley, Chem. Zentr. 1899, ii, 919).

The *methyl acetal of diethylene glycol ether* may be prepared by passing acetylene into a mixture of the mono-ethyl ether of ethylene glycol and mercuric fluoborate (Du Pont de Nemours & Co., and Imperial Chemical Industries, Ltd., B.P. 318980), and by a similar process *glycerylacetal* may be prepared from glycerol and acetylene (B.P. 384332, Du Pont de Nemours & Co.).

Glyceraldehyde ethylacetal,

$$CH_2(OH)CH(OH)CH(OEt)_2,$$

is formed from acrolein (Wohl, Ber. 1898, **31**, 1799).

Furfuraldehyde ethylacetal, b.p. 184°–185°/740 mm., 77°–79°/16 mm. (Adkins, Semb, and Bolander, J. Amer. Chem. Soc. 1931, **53**, 1853).

Acetals derived from ketones may be obtained by the action of the hydrochlorides of formiminoethers or phenylacetiminoethers (Claisen, Ber. 1898, **31**, 1012 ; **40**, 3908 ; Reitter and Hess, Ber. 1907, **40**, 3023).

Acetone methylacetal, $Me_2C(OMe)_2$, b.p. 83°.

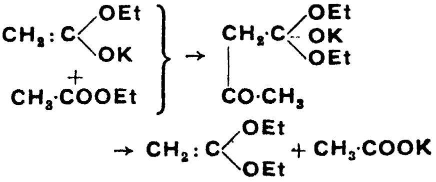
Acetone ethylacetal, $Me_2C(OEt)_2$, b.p. 114°.

Certain saccharides form derivatives termed glycosides (*q.v.*) which are related to acetals. It is probable that the true acetals are intermediate products in their formation :

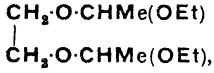
$$HO{\cdot}CH_2{\cdot}[CH(OH)]_x{\cdot}CHO + 2MeOH$$
$$= H_2O + HO{\cdot}CH_2[CH(OH)]_x{\cdot}CH(OMe)_2$$

and these acetals then split off one molecule of alcohol to form the glycosides (Fischer, Ber. 1895, **28**, 1145), which are thus the cyclic-γ-anhydro derivatives of the half acetals of the saccharides.

Keten acetals. In a lapsed patent application by Scheibler (G.P. Anm. Sch. 63789, lapsed Feb., 1926) the inventor claims the production of keten acetals by allowing a solution or suspension of potassio-acetic ester (from potassamide and acetic ester, G.P. 346698) to stand for some hours with a further quantity of the ester :



Complex acetals of use as solvents or softening agents may be prepared by condensing certain organic hydroxy compounds with vinyl ethers of the type $CHR':CR''{\cdot}OR'''$ in presence of acidic catalysts : for example, sym-*di*(*acetaldehyde-ethyl*)-1 : 2-*ethylene acetal*,



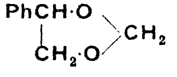
$$\begin{array}{l}CH_2{\cdot}O{\cdot}CHMe(OEt)\\ |\\ CH_2{\cdot}O{\cdot}CHMe(OEt),\end{array}$$

is prepared from vinyl ethyl ether and glycol (B.P. 352474 ; I.G. Farbenind. A.-G.).

The production of *alkoxy-aldehydes* by partial hydrolysis of *alkoxy-acetals* is referred to in B.P. 347943, 348001 (Wacker, Consort. f. Elektrochem. Ind.), the preparation of *methoxy-butaldehyde* from crotonaldehyde and methyl alcohol being given as an example.

Aromatic acetals.—The mono- and di-acetal derivatives of catechol are obtained by heating the monosodium derivative of catechol with monochloracetal (Moreau, Compt. rend. 1898, **126**, 1656).

Jasmine perfumes, which are methenyl acetals of aromatic glycols, may be obtained, according to Verley (B.P. 4779, 1898), from the natural extract of jasmine, which consists essentially of the *methenal of phenylglycol* (Verley, Compt. rend. 1899, **128**, 314) :



or this substance may be synthesised from phenylglycol and formaldehyde. It forms an oil, b.p. 101°/12 mm. The corresponding acetal from acetaldehyde boils at 103°/12 mm.

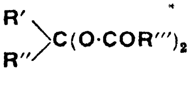
Benzaldehyde ethylacetal, b.p. 217°–223°, prepared by heating benzaldehyde with 1% ethyl alcoholic hydrochloric acid for 60 hours at 100° (Fischer and Giebe, Ber. 1897, **30**, 3053 ; 1898, **31**, 545), or better by heating for 10 minutes under a reflux a mixture of benzaldehyde (37·5 g.), orthoformic ester (57 g.), alcohol (49 g.), and ammonium chloride (0·75 g.); the product after purification with potassium carbonate and fractional distillation yields 62 g. or 97% of theory (Claisen, Ber. 1896, **29**, 1007).

Substances, presumably acetals, are made by condensing a cyclic ketone with a polyhydric alcohol, *e.g.* dextrose with *cyclo*hexanone, or cane-sugar with methyl *cyclo*hexanone (I.G. Farbenind. A.-G., B.P. 385139).

The manufacture of *cyclic acetals* for use in perfumery by condensing a dihydric alcohol with a phenylated aliphatic aldehyde is claimed by I.G. Farbenind. A.-G. in B.P. 346115 ; thus phenylacetaldehyde, condensed with glycol by means of hydrogen chloride, yields glycylphenylacetal, b.p. 115°–120°/12 mm., having a rose odour.

II. Di-acidyl Derivatives of *gem*-Glycols.

Until recent years the diacidyl derivatives corresponding to the true acetals,



$$\begin{array}{l}R'\\ \quad\rangle C(O{\cdot}COR''')_2\\ R''\end{array}$$

(R' and R''=alkyl or hydrogen ; R'''=alkyl), have had no industrial importance. Recently, however, the di-acetyl ester of ethylideneglycol has come into prominence as a means for the production of the large quantities of acetic anhydride required for the manufacture of cellulose acetate.

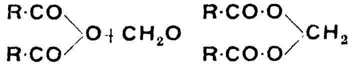
A general method for the preparation of such di-acidyl derivatives is by condensing acid chlorides with carbonyl compounds to form α-chloralkyl fatty esters and these are then treated with silver or potassium salts of the same (or different) acids :

$$RCHCl{\cdot}OAc+Ag{\cdot}OAc=AgCl+RCH(OAc)_2$$

(Schiff, Ber. 1876, **9**, 306 ; Geuther and Rübenkamp, Annalen, 1884, **225**, 273). Acidyl derivatives of methylene glycols can be obtained by treating methylene dihalogenides with the silver salts of fatty acids:

$$CH_2I_2+2AgOAc=2AgI+CH_2(OAc)_2$$

(Butlerow, Annalen, 1858, **107**, 111 ; Arnhold, Annalen, 1887, **240**, 204), or by condensing polyoxymethylenes with acid chlorides or anhydrides in presence of zinc chloride :



$$\begin{array}{l}R{\cdot}CO\\ \quad\rangle O+CH_2O\\ R{\cdot}CO\end{array}\qquad\begin{array}{l}R{\cdot}CO{\cdot}O\\ \quad\rangle CH_2\\ R{\cdot}CO{\cdot}O\end{array}$$

(Descudé, Bull. Soc. chim. 1902 [iii], **27**, 867).

The following more important derivatives may be noted :

Methylene diacetate, $CH_2(OAc)_2$, b.p. 170° (Butlerow, *l.c.* ; Descudé, Bull. Soc. chim. 1902 [iii], **27**, 1215).

Ethylidene diacetate, $CH_3{\cdot}CH(OAc)_2$, m.p. 18·9° ; b.p. 169°, 115°/100 mm. ; d^{15} 1·073, d^{25} 1·070 ; n_D^{25}=1·3985 (Geuther, Annalen, 1858, **106**, 249 ; Schiff, *l.c.* ; Franchimont, Rec. trav. chim. 1882, **1**, 248 ; Geuther and Rübenkamp, *l.c.* ; Société Chimique des Usines du Rhône, G.P. 453021 ; Boehringer and Söhne, B.P. 427448).

Ethylidene dipropionate,

$$CH_3{\cdot}CH(O{\cdot}CO{\cdot}C_2H_5)_2,$$

b.p. 192°, d^{15} 1·020 (Geuther and Rübenkamp, *l.c.* ; *cf. also* B.P. 14246, 1913).

Ethylidene dibutyrate, $CH_3{\cdot}CH(O{\cdot}CO{\cdot}C_3H_7)_2$, b.p. 215°, d^{15} 0·985 (Geuther and Rübenkamp, *l.c.*).

Of these *ethylidene diacetate* is by far the most important. It is now made technically on the large scale by passing acetylene into glacial acetic acid containing a mercury salt as a catalyst. The first stage in the reaction is the production of *vinyl acetate*, which then adds on a second molecule of acetic acid to form the diacetate :

$$C_2H_2+AcOH=CH_2:CH{\cdot}OAc$$
$$CH_2:CH{\cdot}OAc+HOAc=CH_3{\cdot}CH(OAc)_2$$

The vinyl acetate normally formed as a by-product of the reaction may by suitable modifications be made the main product (*see* vinyl acetate).

The original process patented by the

Chemische Fabrik Griesheim-Elektron in 1913 (B.P. 14246, 1913) claims the "production of esters of ethylideneglycol and of vinyl alcohol" by the action of acetylene upon compounds containing carboxyl groups, in the presence of mercury salts: *e.g.* 250 g. glacial acetic acid are mixed with 10 g. mercuric sulphate, and pure dry acetylene passed through at 60°–80° until no further absorption occurs; the product on distillation yields 80–90% of the theoretical amount of ethylidene diacetate.

There have been numerous modifications of the original process, which may be summarised thus:

The necessary catalyst is formed *in situ*: *e.g.* mercuric oxide or a mercury salt of a weak acid is suspended in glacial acetic acid, sulphuric acid is added, and acetylene passed in (Boiteau, B.P. 15919, 1914).

The reaction is carried out in the presence of mercuric acetate and an aliphatic or aromatic sulphonic acid or of sulphuric esters such as methylene sulphate (Soc. Chim. des Usines du Rhône, B.P. 112765, 112766).

The absorption may be effected in presence of strong sulphuric acid, acetic anhydride, and a mercury salt of sulphuric, benzene-sulphonic, naphthalene-sulphonic, or sulphoacetic acids (B.P. 252632), or in presence of mercury and ferric sulphate (B.P. 252640) (Soc. Chim. des Usines du Rhône). According to this patentee the presence of acetic anhydride inhibits the formation of tar, and less mercuric sulphate is required (*cf.* G.P. 453021).

The general process for the production of ethylidene diacetate by passing acetylene into glacial acetic acid containing sulphuric acid with mercuric acetate in suspension is described by Skirrow, Morrison, and Canadian Electro-products, Ltd., in B.P. 308169, 308170, 335223, the special use of mercuric sulphoacetate as a catalyst being protected by B.P. 335223 (*see also* Boehringer and Söhne, B.P. 427448).

An alternative process is described by the Consort. f. Elektrochem. Ind. G.m.b.H. which consists in passing the vapours of the compounds containing the carboxyl group together with acetylene over heated catalysts such as the oxides or salts of cadmium, zinc, mercury, barium, calcium, silver, etc. For instance, acetylene and acetic acid vapour are passed at 200° over charcoal impregnated with cadmium acetate, ethylidene diacetate and vinyl acetate are isolated from the product by fractional distillation (B.P. 182112). The crude ethylidene diacetate may be isolated by agitating with an aqueous solution of sodium acetate or sulphate, and then separating the two layers (Brown and Courtaulds, Ltd., B.P. 353318).

The technical value of ethylidene diacetate, as already noted, lies in the fact that on heating above its boiling-point it breaks down into acetaldehyde (or paraldehyde) and acetic anhydride:

$$CH_3\cdot CH(O\cdot CO\cdot CH_3)_2 = CH_3CHO + O(CO\cdot CH_3)_2$$

Numerous methods for effecting the reaction have been described, amongst them being:-

Ethylidene diacetate is heated above its boiling-point, or heated with catalysts such as sulphuric acid or mercuric sulphate (Bosnische Elektrizitäts A.-G., B.P. 23190, 1914).

Ethylidene diacetate is split up into acetic anhydride and paraldehyde by heating under reduced pressure in presence of acids or acid salts; when a mixture of 400 parts of ester and 8 parts of sulphuric acid (66° Bé) is heated at 70°–80°/100 mm. during 2 hours, 350 parts of a mixture of paraldehyde and acetic anhydride distil over (Soc. Chem. des Usines du Rhône, B.P. 110906, 131399).

In G.P. 451533 (B.P. 238825) the same inventors claim the use of zinc chloride as a catalyst, quoting an example in which 222·2 g. of diacetate gave 61·6 g. (theory 66·9 g.) of acetaldehyde and 151·5 g. (theory 155·2 g.) of acetic anhydride.

A further modification consists in passing the pre-heated vapours of ethylidene diacetate through a glass, steel, or copper tube heated to 300°–400°, the time of contact being 1–6 seconds. Suitable catalysts may be used if desired (Matheson and Canadian Electro-Products, Ltd., B.P. 368835).

Polymerisation of the acetaldehyde produced may be prevented by passing the vapours of the reaction products through a suspension or solution of a metallic acetate in a mixture of ethylidene diacetate and acetic anhydride so as to remove traces of halogen catalysts (*idem.*, B.P. 318960).

Details regarding the Shawinigan plant are given by Morrison and Shaw, Chem. Trade J. 1933, **92**, 415.

AROMATIC ALKYLIDENE DIACETATES.—*Benzal diacetate*, $C_6H_5\cdot CH(OAc)_2$, m.p. 45°–46°, b.p. 225°–230°, can be prepared by heating benzyl chloride with boiling acetic acid in presence of lead peroxide (Bodroux, Bull. Soc. chim. 1899, [3], **21**, 331); by refluxing benzaldehyde with glacial acetic acid and acetic anhydride at 150°–180° (Nef, Annalen, 1897, **298**, 277); or by passing air through a mixture of benzaldehyde and acetic anhydride containing a trace of acetic acid (Freer and Novy, Amer. Chem. J. 1902, **27**, 160). (*Cf. also* Wicke, Annalen, 1857, **102**, 368; Geuther, *ibid.* 1858, **106**, 251; Limpricht, *ibid.* 1866, **139**, 321; Beilstein and Kuhlberg, *ibid.* 1868, **146**, 323; and Zeitsch. f. Chemie, 1867, 277; 1868, 172; Chem. Zentr. 1908, i, 1831; 1909, ii, 1220.) F. A. M.

ACETANILIDE, $C_6H_5\cdot NH\cdot CO\cdot CH_3$, also known under the trade name of *Antifebrin*, is prepared by the acetylation of aniline, by heating aniline with dilute acetic acid or crude pyroligneous acid under pressure at 150°–160° (Matheson & Co., B.P. 6220; D.R.P. 98070). The substitution of thioacetic acid for acetic acid facilitates the reaction (Pawlewski, Ber. 1898, **31**, 661). A laboratory method consists in gently boiling a mixture of equal weights of aniline and acetic acid with 2–3% of zinc chloride under reflux for 3 hours, pouring into water, and crystallising the precipitated acetanilide from hot water; or, more rapidly, by shaking vigorously a cold dilute solution of aniline acetate with acetic anhydride, when the anilide separates in a pure condition.

Acetanilide melts at 114·2° (Reissert, Ber.

1890, **23**, 2243), and boils without decomposition at 303·8° (corr.) (Pictet and Crépieux, Ber. 1888, **21**, 1111), at 305° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1216) ; it is soluble in hot water, alcohol, and ether. Acetanilide is readily hydrolysed on heating with caustic potash or hydrochloric acid, but not by concentrated sulphuric acid at 100° (Hantzsch and Fresse, Ber. 1894, **27**, 2529) ; with zinc chloride at 250° it undergoes condensation to the yellow dye *flavaniline* (Fischer and Rudolph, Ber. 1882, **15**, 1500).

The acetylamino-group is strongly *o*-, *p*-directing ; so that acetanilide readily brominates almost exclusively in the *p*-position, to give p-*bromacetanilide*, also known as *asepsin*, needles or monoclinic prisms, m.p. 166° (Remmers, Ber. 1874, **7**, 346). Nitration in a sulphuric acid solution gives 80% p-*nitroacetanilide*, yellow prisms, m.p. 214° ; and 20% o-*nitroacetanilide*, yellow leaflets, m.p. 93°. These on hydrolysis give the corresponding *p*- and o-*nitroanilines*.

Acetanilide on treatment with a solution of bleaching powder (Chattaway and Orton, Trans. Chem. Soc. 1899, **75**, 1046) or sodium hypochlorite (Barnes and Porter, J. Amer. Chem. Soc. 1930, **52**, 1721) gives N-*chloroacetanilide*, m.p. 91°. In the presence of a mineral acid this rearranges to p-*chloroacetanilide*, colourless needles, m.p. 172°. This rearrangement is of general application ; the halogen enters the *p*-position if it is free, otherwise the *o*-position. These reactions are of great importance in the dyestuffs industry, for obtaining *o*- and *p*-substituted anilines.

The use of acetanilide as a febrifuge is now largely superseded by less harmful preparations, as it acts physiologically by the slow liberation of aniline, which is stated to be oxidised to some extent in the body to *p*-aminophenol.

The following reactions may be used for detecting its presence : (1) bromine water added to a solution of acetanilide in acetic acid gives a white crystalline precipitate of *p*-bromacetanilide, m.p. 168° ; (2) evaporation of a solution to dryness with mercurous nitrate gives a green mass, changing to blood red on addition of a drop of concentrated sulphuric acid ; (3) with acidified potassium dichromate it gives a greenish-blue coloration.

It can be estimated by the usual methods for an acetyl group depending on hydrolysis (Thorpe and Whiteley, "A Manual of Organic Chemical Analysis") ; or by the following method (Seidell, Amer. Chem. J. 1907, **37**, 1091 ; Reclaire, Perf and Essent. Oil Rec. 1921, **12**, 280) : 1·5 g. of substance is boiled with 50 c.c. of 20% hydrochloric acid for 15 minutes, the volume is made up to 500 c.c., and to 25 c.c. an excess of standard potassium bromide-potassium bromate mixture and 5 c.c. concentrated hydrochloric acid are added. Tribromaniline is precipitated, and the excess bromine is estimated by adding potassium iodide and titrating the liberated iodine with potassium thiosulphate (1 c.c. $N/10$ $Na_2S_2O_3 \equiv$ 0·00225 g. acetanilide).

ACETANNIN. *Tannigen.* Acetyltannic acid, obtained by heating tannic acid with acetic anhydride, is nearly insoluble in water, alcohol, and ether. Astringent.

ACETARSOL. *Acetarsone. Stovarsol.* $C_8H_{10}O_5NAs$. 3 - acetylamino - 4 - hydroxyphenylarsonic acid,

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_3(OH)As{\cdot}O(OH)_2,$$

m.p. 240°–250°, almost insoluble in water and alcohol, soluble in dilute alkalis. Used in the treatment of syphilis and malaria (*v.* ARSENICALS, ORGANIC).

ACETARSONE, *Acetarsol* (*q.v.*), *v.* SYNTHETIC DRUGS.

ACETATE SILK DYES. The dyeing properties of acetate silk known in commerce as "Celanese," "Seraceta," or "Rodiaseta," and also of other esters and alkyl derivatives of cellulose, differ markedly from those of fibres composed of pure cellulose, such as cotton, linen, ramie, and the types of artificial silk known as "Viscose," "Cuprammonia," etc. The presence of even 16% of unacetylated hydroxy groups in acetate silks imparts to these fibres a corresponding lack of affinity for direct cotton dyestuffs, whilst they possess only a small affinity for most basic dyestuffs. On the other hand, this type of artificial silk is dyed by colouring-matters having a neutral, weakly basic, or very weakly acidic character, especially when the compounds in question are soluble in organic solvents but insoluble or sparingly soluble in water. It thus appears that the dyeing properties characteristic of acetate silk and its analogues are to be attributed rather to their acting as solid solvents for the dyestuffs in question than to their exerting towards them any chemical affinity.

At the commencement of the manufacture of acetate silk ("Celanese") in England some 20 years ago there were very few available dyestuffs capable of being employed satisfactorily for colouring it, and the difficulties encountered in this direction were so great as to threaten to become a serious bar to its development. To-day there is almost a superabundance of dyestuffs suited to this purpose. Moreover, whereas at the commencement of this period the efforts of technologists were directed to so altering the properties of acetate silk by saponification, etc., that it would take dyestuffs in a similar manner to pure cellulose fibres, it is now realised that the peculiar dyeing properties of this material instead of being a disadvantage constitute a valuable characteristic, since it permits of the ready production of two-colour effects or of coloured patterns upon a white ground in previously woven union materials. For example, a variety of beautiful shot effects can be dyed in the single bath upon materials consisting entirely of artificial silk, of which the warp threads are composed of "viscose" and the weft of "acetate" silk, by making use of a mixture of a direct cotton dyestuff with a suitable colouring-matter having affinity for the acetate silk only. In the production of new dyestuffs of this class the research staffs of the British Dyestuffs Corporation, of the British Celanese Co., and of Scottish Dyes, Ltd., have been the pioneers.

IONAMINES.—These compounds, introduced by A. G. Green and K. H. Saunders in 1922, constituted the earliest class of dyestuffs especially suitable for dyeing acetate silk, whilst having at the same time no affinity for cotton or other pure cellulose fibre. They are prepared by coupling diazo compounds with the methyl-*omega*-sulphonic acid derivatives of primary or secondary amines of the benzene or naphthalene series (B.P. 197809, 200873, 212029, 212030, J. Soc. Dyers and Col. 1923, **39**, 10 ; 1924, **40**, 138). The aminoazo-methyl-*omega*-sulphonates which are thus produced have the general formulæ :

$$X{\cdot}N_2{\cdot}Y{\cdot}NH{\cdot}CH_2{\cdot}SO_3Na$$

and $$X{\cdot}N_2{\cdot}Y{\cdot}NR{\cdot}CH_2{\cdot}SO_3Na$$

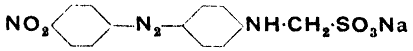
They are yellow to red compounds readily soluble in water. In the hot dye-bath in presence of acetate silk they slowly undergo hydrolysis, more especially upon addition of a small amount of acid or alkali, and give the free aminoazo compounds :

$$X{\cdot}N_2{\cdot}Y{\cdot}NH_2 \text{ or } X{\cdot}N_2{\cdot}Y{\cdot}NHR$$

together with formaldehyde-bisulphite. The aminoazo compounds are insoluble in water, but are taken up by the fibre as they are formed so that the bath remains quite clear throughout the dyeing operation.

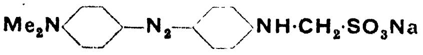
The aminoazo compounds thus fixed upon the acetate silk may be used for direct shades (yellow, orange, or red), or, if derived from primary amines, may be converted by diazotisation upon the fibre and coupling into various other shades. These latter range from red through violet to blue and black, according to the constitution of the original aminoazo compound and the coupling component employed. To avoid loss of lustre by the silk during dyeing, this operation is effected at a temperature not exceeding 65°–75°C., and 1% of formic acid or of sodium carbonate is added to the bath. Diazotisation and development are effected in a manner similar to that employed for diazotisable cotton colours (*e.g.* primuline), except that owing to the lesser permeability of the acetyl-cellulose fibre, more time is required and warm solutions are preferable to cold. The shades obtained are remarkably fast to washing and rubbing, whilst the resistance to light varies with the constitution and is similar to that of direct azo dyestuffs upon cotton. The most satisfactory developer is 2-hydroxy-3-naphthoic acid, by employment of which with different ionamines rich shades of crimson, purple, blue and black are obtainable.

For example, *Ionamine B* is prepared by coupling diazotised *p*-nitraniline with aniline-methyl-*omega*-sulphonic-acid (sulphomethylaniline), and therefore has the constitution :



It dyes orange shades which are converted into red-orange, scarlet or crimson upon diazotisation and development with resorcinol, *β*-naphthol or 2-hydroxy-3-naphthoic acid respectively.

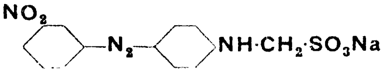
Ionamine Black AS has the constitution :



and is obtained by digesting aminobenzene-azo-dimethylaniline with sodium-bisulphite-formaldehyde. It dyes a yellow shade, which upon diazotisation and development is converted into a deep blue-black.

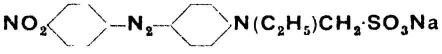
The following are examples of ionamines employed for direct shades without development :—

Ionamine Yellow MA



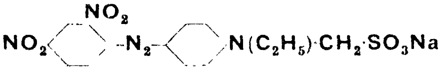
obtained by coupling diazotised *m*-nitraniline with sulphomethyl aniline.

Ionamine Orange GB



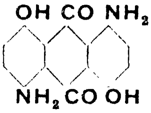
obtained by coupling diazotised *p*-nitraniline with sulphomethyl ethylaniline.

Ionamine Red KA

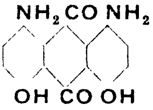


obtained by coupling diazotised dinitraniline with sulphomethyl ethylaniline.

Ionamine Blues.—The principle of introducing sulphomethyl groups in order to confer temporary acidic properties and ready solubility in water is capable of application to other types of dyestuffs besides the azo class. Thus *Ionamine Pure Blues R and G* are prepared from diaminoanthrarufin and diamino-chrysazin respectively :



and

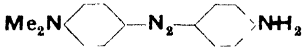


by digesting a suspension of the finely divided base or sulphate with formaldehyde-bisulphite solution (B.P. 23968/99 and 238717). These products dye acetate silk in bright blue shades possessing excellent fastness to washing and a high resistance to light.

Dispersol and S.R.A. Dyes.—Whilst unsulphonated azo compounds such as the Sudans, Oil Yellows, Oil Oranges, etc., have a strong affinity for acetate silk, their insolubility in water rendered their application extremely difficult. This difficulty was overcome by the British Celanese Co. and G. H. Ellis by the employment of these compounds in a colloidal solution or suspension, effected by their incorporation with a soluble oil (sulphonated ricinoleic acid) or other dispersing agent. Mixtures of this class are brought into commerce in paste form under the name of "S.R.A." colours (B.P. 219349, 224925, 273819). For example, a product dyeing acetate silk in bright orange shades is prepared by heating a 25% paste of *p*-nitrobenzene-azo-diphenylamine with an equal weight of Twitchell reagent, obtained by treating a mixture of oleic acid and naphthalene with 20% oleum.

Similar preparations in which other dispersing agents are employed have been introduced by the British Dyestuffs Corporation (Imperial Chemical Industries) under the name of "Dispersol" colours. A striking example of this class is *Dispersol Yellow 3GS*, which is obtained by coupling diazo-benzene chloride with 1 : 3-dihydroxyquinoline (B.P. 236037, *cf.* G.P. 165327/04 and B.P. 11205/05). The compound dyes acetate silk a pure lemon-yellow which does not exhibit "phototropy," a prevalent fault with most of the yellow dyes of the simple azo class.

Dispersol Diazo Black AS probably has the constitution :



Upon diazotisation on the fibre and development with 2-hydroxy-3-naphthoic acid it gives a full bluish-black.

In order to facilitate the dispersion of insoluble azo dyestuffs derived from substituted amines, one or more hydroxyethyl groups may be introduced. The employment of azo derivatives of bases such as di(β-hydroxyethyl) aniline and bis-dihydroxypropylaniline as acetate silk dyes was first mentioned by Green and Saunders (J. Soc. Dyers and Col. 1923, **39**, 10). Dyestuffs of this type are found in both the "Dispersol" series of the I.C.I. and the "Celliton" series of the I.G. Farbenindustrie. The latter corporation have patented the employment of amines such as ethyl-β-hydroxyethylaniline made by acting upon monoethylaniline with ethylene-chlorhydrin. Coupled with diazo compounds derived from components such as *p*-nitraniline and the chloronitranilines, dyestuffs of good fastness ranging from orange-red to bluish-red are obtained : *Dispersol Fast Red R*, *Celliton Red R*, *Celliton Rubine B*, etc.

Certain classes of insoluble dyestuffs other than azo compounds, such as those of the indigoid and indophenol series, may also be employed for dyeing acetate silk if brought into colloidal solution or suspension by means of suitable dispersing agents.

Duranol Dyestuffs.—The products of this class, first introduced by the British Dyestuffs Corporation in 1923, consist of unsulphonated amino derivatives of anthraquinone kept in a state of colloidal solution or suspension by means of dispersing agents (B.P. 211720, 224077, 246984). Similar products were produced by Scottish Dyes, Ltd., under the name of "Celatene" colours, and certain of the "S.R.A." dyes of the British Celanese Co. also belong to this type.

The most suitable dispersing agents for the purpose have been found to be the condensation products of formaldehyde with naphthalene sulphonic acids which are subsequently neutralised with ammonia. The dispersed colouring-matters, like those of the Dispersol type, are sold in paste form. Thus, for example, a dyestuff paste which dyes acetate silk in yellow shades is prepared by incorporating 10 parts of α-aminoanthraquinone with ¼ part or more of dispersing agent and 90 parts of water. The Duranol dyestuffs dye acetate silk directly from a hot bath at about 80°C. They have no affinity for pure cellulose fibres, and therefore can be employed for differential dyeing upon mixed materials in a similar manner to the Ionamines and Dispersols. They exhibit a high degree of fastness to washing and alkalis and for the most part are very resistant to light. The following shades are obtained with various anthraquinone derivatives :

1-Aminoanthraquinone : *yellow.*
1-Amino-2-methyl-anthraquinone : *orange.*
1-Methylamino-anthraquinone : *red.*
1 : 4-Diaminoanthraquinone : *reddish-violet.*
1 : 5-Diaminoanthraquinone : *red.*
1 : 4-Aminohydroxyanthraquinone : *crimson.*
1 : 4-Methyldiaminoanthraquinone : *violet.*
Diaminoanthrarufin and its methyl derivatives : *blue.*
Diaminochrysazin and its methyl derivatives : *bright blue.*
Tetraaminoanthraquinone : *greenish-blue.*
Mixed ureas derived from diaminoanthrarufin or diaminochrysazin with aminoanthraquinone (B.P. 248858) : *brown shades.*

Other Types of Acetate Silk Dyes.—In addition to the foregoing many patents have been taken for the preparation of specific dyestuffs for acetate silk, in which it is sought to confer a sufficient degree of water-solubility in the absence of sulphonic groups, by the introduction of weakly acidic radicles in place of hydrogen atoms in the nucleus or in the amino substituents. This may be effected, for example, by the presence of carboxyl CO_2H, phenylsulphonamide $NH·SO_2Ph$, phthalamic $NH·CO·C_6H_4·CO_2H$, hydroxyethyl $C_2H_4·OH$, or sulphatoethyl $C_2H_4·O·SO_3H$ groupings. It has also been observed that some azo and anthraquinone dyestuffs containing a single sulphonic acid group, if suitably balanced by basic groups, will dye acetate silk satisfactorily. Some of these dyestuffs appear in commerce.

Later Developments.

Since the above article was written (1932), the large increase in the employment of Acetate Silk ("Acetate Rayon") and the introduction of the esters and ethers of cellulose for use as plastics, varnishes, etc., has caused increased attention to be directed to means for colouring these materials. Though many new patents have been filed, development in general has followed closely the lines already laid down. Dyes of many classes have been suggested, but those coming into use are still almost exclusively azo and anthraquinone derivatives. The employment of *omega*-methyl sulphonates of these compounds (*Ionamines*) is now chiefly restricted to the production of fast black shades by diazotisation and development on the fibre, a satisfactory one-bath direct-dyeing black not being yet available.

Both in the azo and anthraquinone classes "solubilisation" is now mainly effected by conversion of the insoluble or sparingly soluble dyestuff into a finely dispersed or colloidal condition by incorporation with dispersing media, such as sulphonated oils, Twitchell reagent, alkylnaphthalenesulphonic acids, higher alcohol sulphuric esters, lignin sulphonic acid, etc.

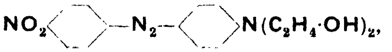
The solubility of both classes of products, azo or anthraquinone, is further increased, and at the same time the affinity for the fibre raised, by the introduction of β-hydroxyethyl (or other hydroxyalkyl) groups in place of methyl or ethyl groups attached to nitrogen. The introduction of butyl groups in a similar position lends increased blueness of shade.

The employment of sulphato derivatives of the type $X{\cdot}N_2{\cdot}Y{\cdot}NH{\cdot}C_2H_4{\cdot}O{\cdot}SO_3Na$ has recently come into prominence for both printing and dyeing acetate silk (Solacet series).

The employment of β-methoxy-ethyl derivatives, $X{\cdot}NH{\cdot}C_2H_4{\cdot}OCH_3$, in place of β-hydroxyethyl compounds, which is said to give faster colours, has been patented by the Society of Chemical Industry in Basle (B.P. 422843).

Azo Class (Dispersol, S.R.A., and dyes of the Celliton, Cibacet, Setacyl, and Artisil series).—Those members of this class which contain hydroxyalkyl groups are now of predominant importance in view of their greater solubility, better affinity and bluer shade.

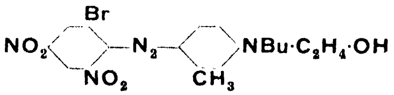
Dispersol Fast Red R (*Celliton Fast Red R*), which has the constitution :



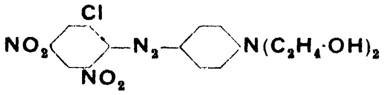
was first described by Green and Saunders (J. Soc. Dyers and Col. 1923, **39**, 11).

The introduction of a second nitro group into the diazo component renders the shade more violet, whilst the blueness, brilliancy and fastness is considerably enhanced by the additional presence of a halogen atom in the 2-position (B.P. 409921, I.G., and 421975, I.C.I.).

Thus the compounds :

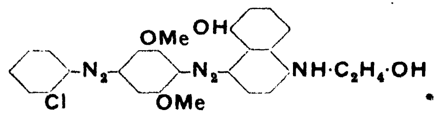


and



are violet dyestuffs of good fastness to light. When the end component is a derivative of α-naphthylamine, blues are obtained (B.P. 319308 and 319390, Brit. Celanese ; B.P. 409921, I.G.).

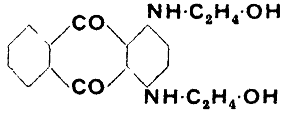
The I.C.I. have developed a range of disazo dyestuffs in which the first component is a derivative of aniline or naphthylamine, the second component dimethoxyaniline, and the end component 1 : 5-aminonaphthol, 1 : 5-hydroxyethylamino-naphthol, or a mono- or dihydroxyethyl-aniline (B.P. 391862, 395005, 395006, 410843, and 422422). The products dye from dispersed solutions giving a range of shades from brown, red and violet to blue, which have good fastness to light and washing. For example the compound :



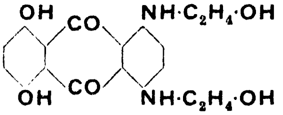
dyes a greenish-blue. If in such a combination the methoxy groups in the middle component are replaced by β-hydroxyethyl groups the affinity and purity of shade are further enhanced. The recently introduced Dispersol Navy Blue RS may possibly belong to this class.

A new idea is disclosed in B.P. 434126 (I.C.I.) which claims the manufacture of mono-azo dyestuffs by employing as coupling components the condensation products of primary amines with three or more molecular proportions of ethylene oxide or of secondary amines with two or more molecular proportions of ethylene oxide. The polyethylene compounds thus obtained are much more readily dispersed in water than the shorter chain hydroxyethyl derivatives, have an enhanced penetration on closely knitted or woven fabrics, and are particularly suitable for printing.

Anthraquinone Class (including Duranols and other dispersed anthraquinone dyestuffs).—Blue dyestuffs are obtained by hydroxyethylation of aminoanthraquinones and aminohydroxyanthraquinones. This can be effected by reacting upon these bases with ethylene oxide (B.P. 11930/1909, 26336/1910, I.G.) ; with ethylene chlorhydrin (B.P. 275636) ; or preferably by heating hydroxyanthraquinones or their leuco compounds with monoethanolamine (B.P. 289807, I.G.). Thus quinizarin heated with a 30% solution of monoethanolamine gives a blue dyestuff of the composition :



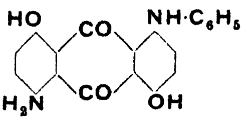
Similarly from leuco-1 : 4 : 5 : 8-tetrahydroxyanthraquinone there is obtained a bluish-green dyestuff having the structure :



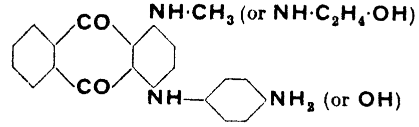
which formula probably represents the constitution of *Celliton Blue Green B.*

Dyestuffs giving clear blue shades of high intensity are obtained also (B.P. 430658, I.G.) by partial alkylation (or hydroxyalkylation) of diaminochrysazin under carefully regulated conditions, using methanol and sulphuric acid, ethylene oxide or ethylene chlorhydrin.

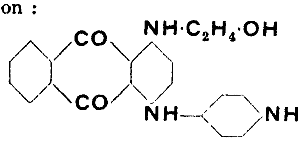
According to patents of the British Celanese Co. (B.P. 416611, 416612, 425591, 420593) dyes of superior fastness to light and to acid atmospheres, especially towards burnt illuminating gas (SO_2), are obtained when in such aminohydroxyanthraquinones there is introduced a phenyl group or an *ortho*methoxyphenyl group. Blue dyes stated to possess exceptional properties are thus obtained from dinitroanthrarufin or dinitrochrysazin by first heating with aniline and then reducing the second nitro group. The product from dinitroanthrarufin has the constitution :



The Society of Chemical Industry in Basle have patented (B.P. 430214) the preparation of analogous products of the type :

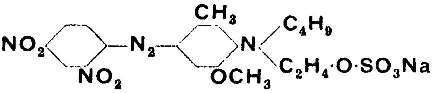


For example a green dyestuff having the constitution :

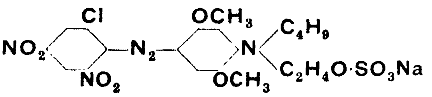


is obtained by reacting upon leucoquinizarin first with *p*-phenylenediamine and then with monoethanolamine in presence of boric acid and an oxidising agent such as arsenic anhydride or lead peroxide.

Sulphato Dyestuffs.—Products containing the labile acid group, $-C_2H_4{\cdot}O{\cdot}SO_3H$, attached to nitrogen have come into prominence recently by reason of their suitability for printing acetate silk materials, giving shades which are readily discharged by reducing agents. Compounds of this class were discovered by Green and Saunders in 1922 (J. Soc. Dyers and Col. 1922, **38**, 227 ; 1923, **39**, 10, 39), and were first applied to the dyeing of acetate silk by Bate and the I.C.I. (B.P. 237739). In the further development of this field by the I.C.I. the following patents have been taken : B.P. 431564 describes the preparation of violet monoazo dyestuffs derived from dinitraniline coupled with sulphato-ethylbutylarylamines, for example :



B.P. 480079 describes the preparation of blue dyestuffs of similar constitution derived from *o*-chloro- (or *o*-bromo-)dinitraniline, for example the compound :



B.P. 429936 describes the preparation of fast brown dyestuffs obtained by coupling diazotised dichloro- (or dibromo-)*p*-nitraniline with ethylsulphato-ethylaniline.

The I.C.I. also obtain greenish-yellow water-soluble dyes having affinity for acetate silk by combining a diazotised *p*-aminoarylhydroxy alkyl ether with *p*-cresol and sulphating the resulting dyestuff by treatment with conc. sulphuric acid (F.P. 792409). A. G. G.

ACETEUGENOL (eugenyl acetate). This substance is present in oil of cloves, and is manufactured synthetically for use in the perfume industry. It has an odour of clove pinks, and is used in compounding artificial carnation perfumes. Formula :

$$AcO{\cdot}C_6H_3(C_3H_5)OCH_3\ ;$$

m.p. 29°, sp.gr. 1·086, ref. index 1·5207, b.p. 282°. Acet-*iso*eugenol, melting at 80°, is a body of similar odour and used for the same purpose. E. J. P.

ACETIC ACID. *Acide acétique, Essigsäure, Acidum Aceticum*, $C_2H_4O_2$, *i.e.* $CH_3{\cdot}COOH$ (B.S.I., Specification 576–1934, Glacial and dilute acetic acid ; B.S.I., Specification 578–1934, Technical acetic acid).

Acetic acid is a normal constituent of certain biological fluids and is also present as the calcium or potassium salt in the juices of plants.

The processes of manufacture may be classified in four main groups :

I. The biological process (including the manufacture of vinegar). II. The destructive distillation of wood. III. Chemical oxidation of alcohol. IV. Synthetic Processes.

I. Biological Production.

There are numerous species of bacteria which, under suitable conditions, are capable of oxidising alcohol through intermediate stages to acetic acid. The best known of these bacteria are *B. aceti*, *B. Pasteurianum*, and *B. Kützingianum* (Compt. rend. Trav. Lab. Carlsberg, 1894 (iii) ; 1900 (v). Other species or possibly varieties of acetic bacteria include Brown's *B. xylinus* (J.C.S. 1886, **30**, 432) and those described by Henneberg, viz. *B. oxydans*, *B. curvus*, *B. xylinoides*, etc. (Zentr. Bakt. 1909, **24**, 13). Although these differ in morphological characteristics, there is reason to believe that some are merely involution forms of others. Certain thermophile bacteria of the acetobacter type are capable of converting cellulose into acetic acid and glucose, without intermediary formation of alcohol, and the principle has been adopted in a number of industrial processes for obtaining acetic acid from waste material such as sawdust. Thus, Power Gas Corporation, Ltd., and Langwell (B.P. 134265, 1918) claim the use of a process of fermenting vegetable matter containing cellulose by inoculating a mash with these bacteria. A similar process has been patented by Tetrault (U.S.P. 1939736, 1932), the fermentation of a mash made from sawdust or the like being effected by special bacteria in the presence of calcium carbonate. The resulting acetic acid is subsequently distilled whilst the glucose remains in the residue. Marine algæ are used as the raw cellulosic material in another process (Darasse Frères and Dupont, B.P. 123325, 1919). Other types of bacteria produce lactic acid in addition to acetic acid, and claim has been made for a process for the production of acetic acid by the agency of a new species (*Lactobacillus acidophilus*) derived from milk (Soc. Anon. des Distilleries des Deux-Sèvres, B.P. 316287, 1929). In the technical production of acetic acid from sawdust in U.S.A., the material is hydrolysed with acid and the resulting wash is fermented by means of special bacteria which yield a mixture of about 10% of acetic acid and 90% of inactive lactic acid, the former being then separated by distillation.

Anaerobic bacteria of a new type isolated from silage or sauerkraut have the property of converting pentoses from hydrolysed wood into acetic and lactic acids without producing ethyl alcohol (Wisconsin Alumni Res. Foundation, B.P. 335596, 1929).

For an outline of the process of making acetic acid from cellulose waste material, *see* Chem. Trade J. 1932, Feb. 5, p. 126.

Acetic Fermentation.—The conditions under which the best yields of acetic acid can be obtained by the action of acetic bacteria have been investigated by Fowler and Subramanyan (J. Indian Inst. Sci. 1923, **6**, 146). Introduction of air under pressure into the fermenting alcoholic liquid was found to increase the yield of acid up to a certain limit depending upon the proportion of alcohol and the amount of bacterial growth. The nature of the bacterial oxidation of primary alcohols to acetic acid has also been studied by Quéré (Compt. rend. 1931, **193**, 445), and the bacterial oxidation of acetaldehyde by Neuberg and Windisch (Biochem. Z 1926, **166**, 454).

Acetic bacteria secrete an enzyme which, when isolated, has the power of oxidising alcohol to acetic acid, and propyl alcohol to propionic acid (Buchner and Gaunt, Annalen, 1906, **349**, 140). Wieland (Ber. 1913, **46**, 3327) found that the enzymic preparation extracted by acetone from the zooglœal pellicle of Hansen's *B. aceti* could be used as a catalyst in the oxidation of alcohol to acetic acid.

The conditions under which acetic bacteria are capable of oxidising alcohol to acetic acid may be varied within certain limits, but the three main requirements are (i) a suitable nutrient medium, (ii) a regulated supply of air, and (iii) the correct temperature, which varies with the species of bacteria from about 90°F. to 112°F. If too much or too little air is supplied the oxidation proceeds irregularly. As soon as the whole of the alcohol has been converted into acetic acid the oxidation will continue and result in the destruction of the acid that has been formed. For a survey of the biochemical activities of the acetic acid bacteria, *see* Chemistry Research Special Report, No. 2, Dept. of Scientific and Industrial Research, 1936.

The so-called "Spirit Acid," or *Essigsprit*, which, until a few years ago, was a common article of commerce, is made by acetifying potato spirit, neutralising the product (containing up to 10 or 12% of acetic acid) with lime, evaporating the mixture, and recovering the acetic acid from the crude calcium acetate by distillation with a mineral acid. The resulting concentrated 80% acid has a pleasant aromatic odour which makes it more suitable for use in food products than the older type of wood acid.

Manufacture of Vinegar.—The term "vinegar" is now applied in most countries to the product obtained by the consecutive alcoholic and acetic fermentations of a saccharine solution, the particular type of vinegar being indicated by a prefix, such as wine vinegar, malt vinegar, cider vinegar, spirit vinegar, etc. In U.S.A. the term "vinegar" without a prefix means cider vinegar. In this country there is no legal standard nomenclature and a product consisting of dilute acetic acid derived from the distillation of wood, or made synthetically, and coloured with caramel, is frequently supplied when "vinegar" is demanded. As the result of deliberations between the Malt Vinegar Brewers' Federation and the Society of Public Analysts in 1934 it was suggested that the term "vinegar" without a prefix should denote "malt" vinegar, and that any vinegar (with or without a prefix) should have been made from whole or unmalted grain saccharified by the action of diastase of malt and subjected to alcoholic and acetic fermentation, without intermediate distillation, with the exception of "spirit vinegar," for which a spirit distilled from an alcoholic wash might be used (*cf.* Analyst, 1935, **60**, 2).

Wine Vinegar.—Although the Orleans process of acetifying wine in casks packed with shavings and provided with holes for the admission of air is still in use in small French vinegar works, it has been largely superseded by the more modern process in which the wine is pumped over a porous medium (wood shavings, vine twigs, etc.) placed upon a perforated false bottom beneath which, in the sides of the vat, small holes are provided for the access of air.

Malt Vinegar.—This is made from malted grain (usually barley) with an admixture of unmalted grain (generally barley, rice or maize).

The first part of the process, the preparation of the wort, is essentially the same as in a distillery. The object of the vinegar maker is to obtain as high a yield of alcohol as possible, and he therefore uses a low-dried malt of high diastatic capacity, and makes the mash at temperatures relatively low, compared with those of mashing in a brewery. After the initial conversion of the starch at about 60°, the goods are sprayed with water at about 65°–70°. In some mashing tuns fitted with rakes a second mash is made, and this has the advantage of effecting conversion of the starch of the grain with less trouble.

In some vinegar works unmalted grain is used, its starch being hydrolysed by means of dilute mineral acid. The grain (usually rice or maize) is mixed with dilute (3%) sulphuric acid in a closed iron vessel and heated under pressure for some hours until the whole of the starch is converted. The contents of the converter are then neutralised with lime and chalk, and the clear supernatant liquid is drawn off, cooled and fermented in the same way as the wort from the mash tun. As a rule sufficient calcium sulphate is left in the liquid to afford an indication that the vinegar was probably made by a conversion process. Vinegar thus prepared might reasonably be described as "grain vinegar."

The wort produced in the mash tun or the converter is cooled over a refrigerator and pitched with yeast as in the brewing of beer, except that a different type of yeast, capable of effecting the maximum attenuation, is used. The temperature at which the fermentation should proceed and the degree of aeration also depend upon the type of yeast. If malt with good diastatic power has been used and efficient aeration is given, there should be no difficulty in attenuating a wort from a sp. gr. of 1·055 down to 1·000 by means of a suitable brewery yeast. On the other hand, still better results may be obtained with a selected bottom-fermentation yeast, in the absence of aeration. After fermentation is complete, usually on the third day, the wash or *gyle*, as it is now termed, is allowed to stand for some days for the yeast to subside, or in some works is filtered before being transferred to the storage vats to await the clarification process.

The secondary or acetic fermentation is effected by the action of one of the species of acetic bacteria mentioned above, which transform the alcohol first into aldehyde and then into acetic acid. Other intermediate products are also formed during the acetification, such as acetal, $CH_3 \cdot CH(OC_2H_5)_2$ (formed by the interaction of the alcohol and aldehyde), and small quantities of ethyl acetate and other esters, succinic and other acids, the nature and amounts of these depending upon the substances (sugars, dextrins, etc.) in the wash.

Theoretically, 46 parts of alcohol yield 60 parts of acetic acid, but in practice there is always a loss. Some years ago this loss ranged from about 10% to as much as 20%, but modern processes of working have not only increased the yield of alcohol from the wort, but have also effected very material reduction in the loss of alcohol and acid during acetification. In some works the loss, compared with the theoretical yield, is only 5% or less.

This loss is due not only to volatilisation of aldehydes and esters, but also to irregular aeration of the porous medium, which has the effect of causing the bacteria to decompose acid already formed.

Insufficient aeration causes the bacteria (in this country usually Brown's *B. xylinus*) to agglomerate into a zoogloeal mass, which may choke the acetifiers and cause serious losses. When once started acetifiers will normally attain their optimum temperature of working. The higher temperatures at which acetifiers work in England, as compared with those on the Continent, may be partly due to acclimatisation of the bacteria. Acetifiers have not undergone any very material changes since the general introduction of the so-called "quick process" some 80 years ago. The acetifiers in many of the works are large vats, some having a capacity of 3,000 gallons; about two-thirds of the way up is a perforated false bottom upon which rest beech shavings or twigs loosely but uniformly packed, to form a bed for the growth of the bacteria. The gyle is distributed in a fine shower by means of spargers which revolve in a space within the top of the vat and, trickling downwards, encounters the upward currents of air, admitted through small holes ranged round the sides of the vat beneath the false bottom.

Many of the improvements suggested for acetifiers have been concerned with the nature of the porous medium. In Luck's apparatus the shavings are replaced by bunches of vertical cords stretched between the distributing tray and the false bottom, and in Singer's apparatus the wash trickles through a series of superimposed rectangular compartments, each of which is filled with wooden tubes packed with porous material, such as charcoal or shavings. In Bersch's rectangular apparatus the acetifying tower consists of a series of frames filled with slats of wood having a space of about ¼ in. between each slat. These frames are superimposed with the slats running in alternate directions and thus afford a very wide area for acetification. They give good results but not the theoretical conversion claimed by their inventor (*cf.* J. Inst. Brew. 1917, **23**, 362). Moreover, they are difficult to clean.

In one of the most modern types of acetifiers shavings are still preferred as the packing material. The beds are very shallow so that they can be rapidly flooded with the alcoholic wash. The excess of liquid is then drained so that the films of wash on the shavings undergo intensive oxidation; the processes of flooding and draining are repeated until the desired degree of acetification has been reached (Ash, B.P. 1948836, 1934).

In Noldin's process (U.S.P. 1610465, 1926) the wash is forced by means of an oxidising gas into the porous medium and is then drawn off, these operations being alternately repeated.

Other improvements in acetifiers relate to the method of distributing the wash. In some of the acetifiers on the flooding system the wash is distributed by means of a siphon, and is drawn off at the bottom into another acetifier, and so on throughout a whole series, thus effecting very rapid acetification without much loss.

The grouping system has been adopted to enable the higher strength of vinegar to be produced rapidly, certain bacteria being acclimatised to the action of 8% and others to 12% acid. This is the method used in the production of *Essigsprit* from potato spirit.

For details of the use of pure cultivations of acetic bacteria in vinegar making, *see* Henneberg, Z. Spiritusind. 1898, 1808, and Zentr. Bakt. 1905, **14**, 681; Rothenbach, Woch. Brau. **15**, 445; Deut. Essigind. 1905, **9**, 217; Mayer, Z. Spiritusind. **21**, 334; Buchner and Gaunt, Annalen, 1906, **349**, 140.

An obvious means of preventing some of the loss that occurs during acetification is to connect the air-outlets with a condenser, and various devices on these lines have been proposed. In some of these, tubes from the top of the acetifiers lead into a common main surrounded by a cooling jacket. Steinmetz's device (G.P. 443802, 1925) is a condenser with hollow plates through which water circulates, and is fitted into the upper space of individual acetifiers. In other types of apparatus (*e.g.* that of Fox, B.P. 293539, 1927) the vapours are led into atmospheric condensers outside, and the condensed liquid is returned to the acetifier. In Fring's device (B.P. 296950, 1928) the spent-air duct is connected with siphon-tubes which periodically deliver the correct quantities of wash to the acetifier.

After completion of the acetification the wash is drawn off into store vats where it is allowed to stand for some weeks at least, in order to develop an aroma and to deposit suspended matter. In some works clarification is accelerated by the addition of gelatin finings or, if iron has gained access to the vinegar, potassium ferrocyanide is sometimes added. Apparently no hydrocyanic acid is formed although, as Harden pointed out (L.G.B.

Report on Vinegar, 1908, p. 27), there is a possibility of its being liberated if too much ferrocyanide is added.

The old method of filtration through filter beds of sand, shingle and beech chips, technically termed *rapes*, has been superseded by the use of compact filters in which cellulose pulp or finely divided siliceous earth (kieselguhr) forms the filtering medium. Finally the "bright" vinegar, which will contain about 6% of acetic acid, is diluted to the required strength with water, and usually coloured with caramel. The various strengths are technically known in the industry as Nos. 16, 18, 20, 22, and 24. (For a discussion of the origin of these terms, *see* Mitchell, "Vinegar. Its Manufacture and Examination," 2nd Ed., Griffin, London, 1926.)

Distilled Vinegar.—Malt vinegar is distilled under reduced pressure, generally in small stills made of gun-metal lined with tin. Distillation at the ordinary atmospheric pressure gives a distillate with an unpleasant flavour. The distillate is usually condensed by means of a tin coil cooled in running water, and is diluted to the strength required by the trade. It is sold under the names of *distilled malt vinegar, distilled vinegar, white vinegar,* and (incorrectly) *white wine vinegar.*

Cider Vinegar.—Cider vinegar, which is the vinegar mainly used in U.S.A., is pale yellow in colour, has sp.gr. from about 1·013 to 1·015, and on evaporation leaves a gum-like residue (1·5–1·8%) having an odour of baked apples and containing malic but not tartaric acid. The acetic strength ranges from 3·5 to over 6% and the ash is not less than 0·25% and contains no soda, whereas the ash from factitious cider vinegars contains a large proportion of lime and soda (Doolittle and Hess). For other characteristics of cider vinegar, *see* Smith, J. Amer. Chem. Soc. 1898, **20**, 3 ; Leach and Lythgoe, *idem.* 1904, **26**, 375 ; van Slyke, New York Agric. Exp. Stn. Bull. 1904, **258**, 439 ; Ladd, N. Dakota Exp. Stn. Bull. **32**, 278 ; Tolman and Goodnow, Ind. Eng. Chem. 1913, **5**, 928.

Date Vinegar is made from an infusion of dates by consecutive alcoholic and acetic fermentations. Compared with malt vinegar, it is low in phosphoric acid and nitrogen.

Spirit Vinegar.—This is made by acetification of spirit derived from potato starch (in Germany) or from the spirit distilled from fermented molasses (in England). Spirit vinegar yields only a trace of total solids, but differs from wood vinegar in containing an appreciable amount of alcohol (sometimes 0·2%).

Other vinegars in limited demand include *perry* and *crab-apple vinegar*, used in Wales and Monmouthshire, *banana vinegar* (*see* von Loesecke, Ind. Eng. Chem. 1929, **21**, 175), and *raspberry vinegar,* which is usually a heavy raspberry syrup made acid by the addition of distilled vinegar.

Glucose or Sugar Vinegar is not sold under that name, but brewing sugar, molasses, or glucose are sometimes used without declaration, as substitutes for grain in the manufacture of vinegar afterwards sold as "malt vinegar." Although vinegars made from sugars alone are very low in proteins and yield an ash largely composed of potassium salts and often rich in sulphates, the problem is usually not one of distinguishing between a malt vinegar and an all-sugar vinegar, but of detecting an admixture. The abnormal chemical characteristics of the reputed malt vinegar may have an explanation other than adulteration of malt vinegar with sugar vinegar.

Wood "Vinegar," as its name suggests, is a product made from diluted acetic acid coloured with caramel. Since, however, a large proportion of the commercial acid now sold is of synthetic origin, the term "artificial vinegar" is often a more correct description than the older term. Some of the artificial vinegars on the market contain a small proportion of malt extract or are flavoured with ethyl acetate to give a closer imitation of the brewed product. They contain from about 0·2–0·6% of solid matter, yield 0·02–0·04% of ash, and usually contain insignificant amounts of phosphoric acid and nitrogen. If synthetic acid has been used in their production, they may contain traces of mercury.

An artificial product termed *vinegar essence* is also sold. This consists of acid of 50–60% strength coloured with caramel in sufficient quantity to give the correct colour when diluted with water to the strength of a 4% vinegar. Malt extract and ammonium phosphate are also sometimes added to the product.

An ordinary malt vinegar contains only about one-tenth of its total nitrogen in the form of ammoniacal nitrogen, therefore the addition of ammonium salts may be readily detected (*see* Mitchell, Analyst, 1931, **56**, 178).

Although there is no legal standard for the acetic strength of either brewed vinegar or artificial vinegar, it is now commonly accepted by the trade that the amount shall not fall below 4%, and there have been numerous convictions for the sale of weaker products.

Characteristics of Vinegars.—The table on p. 47 gives analyses of vinegars typical of those sold as "malt vinegar" about 10 years ago. Of these samples, Nos. I and II were typical of normal malt vinegar and are still representative of the products of some vinegar works. No. III was the product of a mixture of rice with green malt (sprouted barley with the rootlets still attached). No. V was low in solid matter (phosphoric acid and nitrogen and was probably adulterated) ; and No. VI was made by the conversion process.

The following analyses are typical of malt vinegar made at the present time from mixtures of malted and unmalted grain by processes in which the manufacturing losses which formerly occurred have been largely eliminated.

No.	Sp. gr. at 15·5°.	Acetic acid %	Non-volatile acid (as lactic acid) %	Ash %	P_2O_5 %	Nitrogen %
I	1·0148	5·06	0·29	0·27	0·054	0·08
II	1·0155	4·34	0·22	0·36	0·057	0·06

These results show that Hehner's method of calculation from the "original solids" of a

No.	Sp.gr. at 15·5°.	Acetic acid.	Total solids.	Ash.	P_2O_5.	Nitrogen.	P_2O_5 on original solids.	Nitrogen on original solids.
		%	%	%	%	%	%	%
I.	1·0175	5·4	2·74	0·49	0·07	0·07	0·69	0·64
II.	1·021	5·4	3·84	0·39	0·13	0·14	1·08	1·23
III.	1·0145	5·1	1·68	0·16	0·03	0·03	0·32	0·28
IV.	1·021	5·9	3·67	0·34	0·04	0·14	0·34	1·11
V.	1·013	4·5	1·75	0·24	0·09	0·08	1·00	0·90
VI.	1·014	4·3	2·04	0·47	0·07	0·06	0·83	0·70

vinegar can no longer be relied upon, now that the loss on acetification has been so materially reduced.

Wine vinegar varies in colour from pale yellow to reddish-yellow or red. It usually contains from 6 to 8% of acetic acid, with 1·7–2·4% of total solids, and has sp.gr. of about 1·014–1·015 at 15°. About 0·25% of potassium tartrate is usually present.

Analysis of Vinegar.—The total acidity of vinegar is usually determined by titration with standard alkali (phenolphthalein as indicator). The fixed acidity remaining after removal of volatile acid is commonly expressed as lactic acid.

Formic Acid is frequently a constituent of commercial acetic acid and thus may be present in vinegar that has been adulterated with acetic acid (Kreutz and Buchner, Z. Unters. Lebensm. 1926, **52**, 295). It may be determined in spirit vinegar or distilled vinegar by Klein's method (Chem.-Ztg. 1908, **32**, 815), in which the sample is neutralised with alkali and titrated with permanganate. Since caramel may contain formic acid and grain vinegars contain substances which reduce permanganate, the method cannot be applied to malt vinegar.

Tartaric Acid is determined by converting it into potassium hydrogen tartrate, which is then titrated (*cf.* Z. anal. Chem. 1908, **47**, 57). A method of identifying wine vinegar has been based on the forms of calcium tartrate obtained under various conditions (Patzauer, Chem.-Ztg. 1933, **57**, 735 ; Pritzker, *idem.* 1933, **57**, 927).

Total Solids.—A measured quantity of vinegar is usually evaporated to dryness at 100°. This does not give the true value, however, for Laudig (J. Assoc. Off. Agric. Chem. 1927, **10**, 520) has shown that for the complete removal of acetic acid from the total solids it is necessary to repeat the evaporation three times and finally to dry the residue for 2½ hours in the steam-oven.

Alkalinity of Ash.—The following results obtained by Allen illustrate the way in which the alkalinity of the ash may sometimes afford an indication of the origin. A glucose vinegar, for instance, will show a low proportion of potassium oxide owing to the mineral acid used for the hydrolysis having combined with part of the bases.

Alkalinity (as K_2O % on the vinegar).

Vinegar from malt and grain.	Vinegar from grain and sugar.	Vinegar from rice.	Sugar vinegar.
0·091–0·118	0·03	0·013	trace

Free Mineral Acids.—These are no longer added to vinegar. In the improbable event of sulphuric acid being present the method of Richardson and Bowen (J.S.C.I. 1906, **25**, 836) may be used for calculating the amount originally added.

Combined Sulphuric Acid.—Amounts greater than the normal figures (0·03–0·17%) are usually due to the vinegar having been made by the conversion process.

Phosphoric Acid (P_2O_5).—A convenient method of determination is to dissolve the ash from 10 ml. of the vinegar in dilute nitric acid and to add a large excess of molybdic reagent. The yellow precipitate is washed twice by decantation with cold water and dissolved in dilute ammonia, and the solution is evaporated. The weight of the residue, divided by 28·5, gives the amount of phosphoric acid (P_2O_5).

Nitrogen is conveniently determined by Kjeldahl's method.

Caramel.—Added caramel may often be precipitated by fuller's earth, but different earths vary in their precipitating power (Dubois, J. Amer. Chem. Soc. 1907, **29**, 75).

Sulphur Dioxide.—Under the Public Health (Preservatives, etc., in Food) Regulations made by the Minister of Health, as amended 1927, vinegar may not contain any sulphur dioxide. Cox, however (Analyst, 1927, **52**, 397), has shown that malt vinegar can contain from 10 to 20 p.p.m. of sulphur dioxide derived from the malt or caramel, or from 20 to 60 p.p.m. if the vinegar has been kept in sulphured vats or casks. For methods of determining sulphur dioxide, *see* Aerated Waters.

Metallic Impurities.—Iron is usually present in most vinegars ; if present in excess, it causes persistent cloudiness. It may be detected by adding potassium ferrocyanide directly to the vinegar. Other metals likely to be present include copper and tin. For the detection and determination of these when present in traces, and for the determination of arsenic, *see* Aerated Waters.

Optical Standard for Vinegar.—Vinegar made from malt is dextrorotatory, and the U.S.A. Dept. Agric. (Circular No. 19, 1906) therefore required all malt vinegar to be dextrorotatory. It was shown by Chapman, however (Analyst, 1912, **57**, 123), that some pure grain vinegars show a lævorotation.

II. Destructive Distillation of Wood.

The yields of acetic acid obtainable by the direct destructive distillation of wood do not vary greatly with the species of tree. Thus, Hawley and Palmer (Eighth Int. Cong. Appl. Chem. 1912, (4), Orig. Comm. 6, 138) obtained the following average results calculated on the dry material: Birch, 6·50; beech, 5·55; maple, 4·95; red gum, 5·16; chestnut, 5·32; hickory, 4·61; oak, 4·70%. Increasing the temperature within the retort above 320° had no material influence upon the yield.

Hydrolysis of Wood.—Acetic acid is one of the products obtained by boiling sawdust with water in an autoclave under a pressure of 6 atm. Yields of 1·17–1·37% were thus obtained by Bergstrom (Papier-Fabr. 1913, **11**, 305) from spruce and pine, and more than twice as much from deciduous woods. On the other hand, the conifers yielded more formic acid (0·19–0·23%) than the deciduous woods. Destructive distillation of the two classes of woods gave analogous results, and acetate of lime made from birch or other deciduous woods was found to contain less formic acid than that prepared from the wood of conifers.

It was found by Pringsheim and Magnus (Z. angew. Chem. 1920, **33**, 56) that beechwood lignin gave much higher yields of acetic acid than that of other deciduous woods when hydrolysed with 3·5% sodium hydroxide solution under pressure (*e.g.* 37·8 and 19·9% respectively). In analogous experiments Padovani and Mariotti (Annali Chim. Appl. 1930, **20**, 203) obtained 6·6% of acetic acid in the hydrolysis of beechwood with cold sodium hydroxide solution under a pressure of 5 atm. Beechwood, submitted to ordinary destructive distillation, yielded 4·5% of acetic acid.

In another process sulphurous acid and steam are used as the hydrolysing agents (Raisin, F.P. 446871 and 446878, 1911), the resulting acid vapours being condensed and neutralised with sodium hydroxide.

Lignite and other forms of coal are used as the raw material for the production of acetic acid by destructive distillation (Behrens, G.P. 275049, 1913).

In Rawling's process (U.S.P. 1695742, 1928) sodium acetate is prepared from the sulphate liquors in the pulping of wood, the extract being concentrated, treated with sodium hydroxide and lime at 200°–280°, and filtered, and the sodium acetate recovered from the filtrate.

Distillation of Acetic Acid.—Prior to the introduction of synthetic acetic acid the best *glacial* acid was termed "soda acid," from the fact of its being obtained from anhydrous sodium acetate, by distillation with the calculated proportion of sulphuric acid or with potassium or sodium bisulphate.

Another source of concentrated acid is the commercial crude "grey" or "brown" acetate of lime which is obtained by neutralising the acetic acid fraction from the destructive distillation of wood. This acetate is distilled with dilute sulphuric acid, and the resulting *pyroligneous acid* (which has a pronounced tarry odour) is purified by treatment with an oxidising agent (*e.g.* permanganate) and fractional distillation. A purer acid is obtained from calcium acetochloride, $CaC_2H_3O_2Cl,5H_2O$, which is obtained by treating a solution of the commercial "acetate of lime" with calcium chloride, and recrystallising and purifying the salt that separates. The crystals are distilled with dilute sulphuric acid, and the acid is concentrated as described above.

A method of eliminating, to a large extent, sulphur dioxide in the distillate is claimed by Farbenfabriken vorm. F. Bayer & Co. (G.P. 220705, 1907). The crude acetate is heated to about 130° in the still, and the pressure is then reduced before introducing the sulphuric acid.

Distillation under reduced pressure is also used in Haggenmacher's process (U.S.P. 1463209, 1923), the acetate being distilled with less than 1 mol. proportion of hydrochloric acid, and the distillate purified and redistilled with steam and hydrochloric acid.

In Fauque's process (F.P. 612595, 1926) crude acetate of lime is made into a paste with water, and saturated with gaseous hydrogen chloride in a tower packed with stoneware. The mass is warmed until it becomes liquid and, after the addition of calcium acetate equivalent to the excess of hydrochloric acid introduced, is distilled, leaving a residue of tarry matter and calcium chloride.

Andreau's method (U.S.P. 1381782, 1921), which is claimed to yield nearly anhydrous acid, consists in suspending the acetate in paraffin oil, adding sulphuric acid, and distilling the acetic acid.

Various continuous processes of distillation have been devised, such as that of Prager (F.P. 449035, 1911), in which the acetate is placed in a series of compartments and, after being progressively sprinkled with sulphuric acid, is automatically transferred from one compartment to the next while the liberated acetic acid vapours are condensed in the upper part of the apparatus.

In another continuous process (Brauer, U.S.P. 1196329, 1916) a mixture of acetate and sulphuric acid is mechanically spread over a heated rotating surface from which the residue left after condensation of the acetic acid is removed by scrapers.

An electrolytic method of destroying impurities has been devised by French (U.S.P. 1104978, 1914), whilst Gorhan (U.S.P. 1210792, 1917) destroys formic acid by treating the crude acetic acid with an equal weight of 70% sulphuric acid prior to redistillation.

Concentration of Acetic Acid.—Great advances have been made during the last few years in the methods of separating the acetic acid from the other products of the destructive distillation of wood and numerous processes have been devised for the direct distillation of the pyroligneous acid, the elimination of the intermediate production of acetate of lime and the concentration of acetic acid in the final distillate.

Among the processes whereby pure acetic acid is obtained in one operation by distillation in special fractionating columns is that of Charles (*see* Chem.-Ztg. 1931, **55**, 881). Another extensively used process is that of Suida (B.P. 218271–2, 1924; F.P. 594925, 1925), in which a liquid not readily miscible with water but which will absorb acetic acid is made to trickle down an extraction column where it meets the acetic acid vapours. The resulting solution is afterwards submitted to fractional distillation. In practice, the tar in the pyroligneous acid obtained by the destructive distillation of wood is allowed to subside in a settling tank, and is subsequently distilled with steam, the lighter oils in the distillate being used as fuel, whilst distillation of the heavier oils and the residue yields a solvent oil which can be used for extracting the acetic acid from the crude pyroligneous acid. In one modification of the process, used by the Crossett Chemical Co., U.S.A., methyl alcohol is recovered after removal of the acetic acid. Details of the Suida process, as used in another U.S.A. works, have been given by Krase (Chem. and Met. Eng. 1929, **36**, 657). According to Poste (Ind. Eng. Chem. 1932, **24**, 722), 250 gallons (Amer.) of crude pyroligneous acid are obtained from one cord (4,100 lb.) of average hard wood, and by the use of the Suida process the yields of saleable products are as follows : charcoal (15·5% volatile), 1,330 lb. ; oil (wood-preserving, etc.), 4·5 gallons ; pitch, 40–45 lb. ; acetic acid (100% basis), 120 lb. ; methanol (100% basis), 9 gallons.

The solvents claimed for extracting acetic acid from crude pyroligneous acid include the following : dichloroethylene (Galitzenstein, Z. angew. Chem. 1916, **20**, 148) ; a petroleum distillate (*e.g.* spindle oil) by the British Cellulose and Chemical Manufacturing Co. and W. Bader (B.P. 204196, 1922) ; ether by Brewster (B.P. 187603, 1922) ; butyric acid by Piron (U.S.P. 1477076, 1923) ; hydroxylated compounds boiling above 150° (*e.g.* cresols), or liquid fatty acids with b.p. about 150°, by Suida (B.P. 230447, 1925) ; solvent with b.p. between 120° and 150° (*e.g.* amyl acetate) by Soc. Anon. des Distilleries des Deux-Sèvres (B.P. 296974, 1928) ; a halogenated hydrocarbon (trichloroethylene) by I.G. Farbenind. A.-G. (B.P. 3000923, 1930). According to Partridge (Ind. Eng. Chem. 1931, **23**, 482) extraction with *iso*-propyl ether is capable of yielding practically anhydrous acetic acid. Modern plant, with increased rectifying capacity, produces acid of 90–95% strength. The methyl alcohol is carried through the extraction columns in the form of vapour and subsequently condensed.

In the process claimed by Brit. Celanese, Ltd., Oxley, and Fallows (B.P. 356741, 1930), vapours of the entraining liquid are led into the dilute acid, or are mixed with the vapours of the dilute acid, and then fractionally distilled. Suitable liquids mentioned include benzene, xylene, di- or tri-chloroethylene, ethyl acetate, etc.

In Wacker's process (B.P. 298137, 1928) butyl acetate or other ester with b.p. between 105° and 133° is used as the concentrating agent. The process claimed by I.G. Farbenind. A.-G. (B.P. 284588, 1928) employs an analogous method of separation; the dilute acetic acid is mixed with ethyl acetate and distilled, and the distillate (a mixture of the ester and water) is distilled at 69°–70°, the ester being returned to the still and the process repeated until all water has been removed, after which the ester is distilled, leaving a residue of glacial acetic acid.

Concentration by Adsorption.—Certain processes of concentration have been based on adsorption of the acetic acid. Thus, in the process claimed by Imperial Chemical Industries, Ltd., and Leicester (B.P. 332983, 1929) acetic acid is selectively adsorbed by activated carbon at 120°–130°, and may be recovered in a concentrated form by heating the carbon at 200°. For details of a study of the best conditions for the adsorption (on silica gel) of acetic acid from its solution in petroleum oil (gasoline), *see* Jones, Z. physikal. Chem., 1925, **29**, 326.

Removal of Water.—The use of preferential adsorbents for the water in dilute acetic acid is claimed in several processes. Thus, Farbenfabr. vorm. Bayer & Co. (G.P. 314943) dissolve an alkali bisulphate in the dilute acid, then extract the acid with ether and distil the extract, whereby a residue containing 70–80% of acetic acid is left. In Lichtenthaeler's patents (U.S.P. 1492717–8, 1924) anhydrous ammonium alum is used as the adsorbent. After adsorption of the water by hydration of an anhydrous salt, volatile substances are removed in a current of gas and condensed (U.S.P. 1817993, 1931). In the process claimed by Dreyfus (B.P. 338187, 1929) water is separated by adding a hydrocarbon, halogenated hydrocarbon, or other substance capable of precipitating it, leaving a more concentrated supernatant acetic acid. Other substances claimed for the adsorption of water include anhydrous copper sulphate (Chem. Fabr. Griesheim-Elektron, G.P. 230171, 1909) and metaphosphoric acid (G.P. 282263, 1914). In another process (Harburger Chem. Werke Schön & Co., G.P. 292959, 1915) the dilute acid is treated with potassium acetate, and the resulting double compound is separated and redistilled.

Concentration by Freezing.—Concentration of dilute acetic acid may be effected by chilling the liquid to −26° (the eutectic point of acetic acid—water), when ice crystals separate. In a process claimed by I.G. Farbenind. A.-G. (B.P. 312173, 1929) the acid thus concentrated is separated by causing it to form a double compound with a substance such as carbamide or potassium acetate. This double compound is separated by freezing, and glacial acetic acid is recovered from it by distillation *in vacuo*.

In the process claimed by Distillers Co., Ltd., Langwell, and Gilmour (B.P. 378463, 1931), the dilute acid is chilled to −2°, and made to flow through a heat-exchanger, whereby free ice-crystals are carried forward and deposition of ice-crusts is prevented. Vinegar can thus be concentrated in two operations to a strength of 40% of acetic acid while retaining its flavour and aroma.

III. Chemical Oxidation of Ethyl Alcohol and Acetaldehyde.

In the earliest methods of oxidising alcohol to acetic acid, platinum was used as a catalyst, and the methods were too expensive to be much employed on a manufacturing scale. In Behrens' process (B.P. 28839, 1910) the alcohol is oxidised to aldehyde in the presence of zinc oxide as catalyst at about 350°, and the aldehyde is then oxidised by contact with oxygen in an absorbing tower.

In another process claimed by the Chem. Fabr. Griesheim-Elektron (B.P. 17424, 1911) acetaldehyde is oxidised by means of air in presence of acetic acid or a chlorine derivative thereof and a catalyst (*e.g.* vanadium pentoxide or uranium oxide); or the aldehyde may be oxidised by oxygen in excess (B.P. 8076, 1912).

The use of manganese compounds is claimed to promote the oxidation without risk of explosion, as may occur when compounds of vanadium, chromium, or cerium are used (Consort. f. Elektrochem. Ind., F.P. 460971, 1913).

A method of oxidising acetaldehyde with oxygen under pressure in presence of 1% of ceric oxide or other catalyst is claimed by Farbw. vorm. Meister, Lucius & Brüning (B.P. 10377, 1914). In Hibbert's process (U.S.P. 1230899, 1917) wood charcoal previously saturated with acetic acid is used as the catalyst.

In Maxted's process (B.P. 238033, 1924) a mixture of vaporised alcohol and oxygen or air is passed over metallic vanadates (preferably of tin) at a temperature above 300°.

Dreyfus (B.P. 341031, 1929) claims the use of a process in which alcohol and oxygen, preferably in the presence of steam, are passed over an oxide, hydroxide or carbonate of a metal, other than an alkali or alkaline earth metal, at 280°–300°. In another process (B.P. 347323, 1930) acetaldehyde is oxidised with oxygen at 60°–75° in a mixing vessel.

During the chemical oxidation of acetaldehyde the formation of the explosive peracetic acid is prevented by the addition to the catalyst of a large amount of a hydrated salt (*e.g.* ferrous sulphate) (H. O. Traun's Forschungslab., B.P. 156146, 1920). The oxidation process of Brit. Celanese, Ltd., Thomas, and Groombridge (B.P. 367863, 1930), makes use of a manganic salt (preferably the acetate) as a catalyst. In B.P. 368348, 1930, a continuous process of oxidation is described.

IV. Synthetic Processes.

Acid made from acetylene, methane, etc., has to a large extent replaced the acid derived from wood. The conditions for obtaining the best yields from acetylene have been studied by Neumann and Schneider (Z. angew. Chem. 1920, **33**, 189), and a detailed description of an industrial process has been published by Pascal (Mém. Poudres, 1926, **22**, 1; Ber. 1926, **59** [B], 767).

In one of the earliest processes (F.P. 360249, 1905) acetylene is passed into a solution of a mercuric salt, mercury acetylide being precipitated. On boiling the liquid, aldehyde is formed and mercury precipitated; the aldehyde is then oxidised.

The process of Farbenf. vorm. Bayer & Co. (F.P. 467778, 1913) depends on electrolytic oxidation of the acetylene in presence of a mercury compound. In another patent of the same firm (F.P. 467515, 1914) the acetylene is passed through a solution of hydrogen peroxide or a persulphate at 30°–40° in presence of mercury or a mercury compound. In another process the use of catalysts other than mercury and also the application of pressure are claimed (F.P. 471253, 1914).

Direct oxidation of acetylene to acetic acid without intermediate formation of acetaldehyde is claimed in a process of Chem. Fabr. Griesheim-Elektron (F.P. 473158, 1914), the oxidation being effected by oxygen in an organic acid medium in presence of water and a catalyst, such as iron oxide or vanadium oxide.

Many of the subsequent patents are concerned with the use of special catalysts. For instance, acetaldehyde vapours, obtained by the catalytic hydration of acetylene (B.P. 124194, 1919), are polymerised to paraldehyde by the use of a catalyst consisting of sulphuric acid containing mercury, ferric, or vanadium salts, and the paraldehyde is depolymerised, and oxidised to acetic acid by means of oxygen, with copper permanganate as catalyst. Other catalysts for converting acetylene into acetaldehyde include solutions of mercury salts containing ferrous salts (G.P. 309103–4, 1916), china clay (Soller and Hotz, B.P. 154304, 1919), kieselguhr (Farbenf. vorm. Bayer & Co., G.P. 336021), cellulose and wood sawdust activated with steam (Kárpáti and Hübsch, B.P. 287135 and 294226, 1928), nitrogen oxides (B.P. 376045, 1931), boric anhydride and a non-volatile acid, such as H_3PO_4 (Horsley and I.C.I., Ltd., B.P. 351016, 1930).

Special processes and forms of apparatus are also claimed by Matheson (B.P. 154368, 1919), Traun's Forschungslab. (B.P. 156147, 1920), and I.G. Farbenind. A.-G. (304855, 1927).

In the process patented by Riley and I.C.I., Ltd. (B.P. 346883, 1930) a catalyst of mercury sulphate and ferric sulphate is used in the hydration of acetylene to acetaldehyde, the activity of the catalyst being maintained by withdrawing part of the liquid and oxidising the ferrous sulphate with oxygen before returning it to the circuit.

Acetic Acid from Methane.—Dreyfus (B.P. 226248, 1923) claims a process of producing acetaldehyde and acetic acid by submitting a mixture of methane and a carbon oxide or oxides to pressure below 500° in contact with a catalyst (*e.g.* nickel carbonate).

Acetic Acid from Methyl Alcohol.—Several processes have been patented. Brit. Celanese, Ltd., Bader, and Dreyfus (B.P. 283989, 1926) obtain a mixture of acetic acid and methyl acetate by treatment of methyl alcohol with carbon monoxide with or without hydrogen at 300°–400° in presence of a catalyst (an inorganic acid or acid salt, *e.g.* phosphoric acid). Catalytic action is promoted by the addition of a copper salt, *e.g.* copper phosphate (B.P. 317867, 1928). In another process a mixture of methyl alcohol and oxygen (or air) is passed into the bottom of a coherent column of acetic acid containing a catalyst maintained at 50°–70° (Johnson, B.P. 405719, 1932), and in Patterson's process (B.P. 405282, 1932) a mixture of carbon monoxide, methyl alcohol and water vapour is passed over hydrated tungstic oxide at 300°–400°.

For a study of the condition underlying the synthetic production of acetic acid from methyl alcohol and carbon monoxide, *see* Shilov, J. Chem. Ind. Russia, 1930, **7**, 110; B, 1932, 12; and for a discussion of such factors as temperature, space, velocity, composition of reacting substances, and recirculation of by-products, *see* Singh and Krase (Ind. Eng. Chem. 1935, **27**, 909).

Acetic Acid from Methyl Formate.—In a process claimed by Dreyfus (B.P. 259641, 1925) the vapour of methyl formate is converted into acetic acid by heating it under pressure at 400°–450° in contact with a catalyst (*e.g.* an oxide of copper).

Acetic Acid from Formaldehyde.—A mixture of formaldehyde vapour and carbon monoxide is heated under high pressure at 300°–400° (Brit. Celanese, Ltd., Green, and Handley, B.P. 334189, 1929).

Acetic Acid from Carbon Monoxide.—Acetic acid is obtained by hydrogenating carbon monoxide at 500°–540° in the presence of catalysts, such as phosphates, silicates, or borates of nickel, cobalt, chromium, iron or copper (Soc. Franç. de Catalyse Génér., B.P. 338329, 1929).

Synthetic Production of Esters.—Methyl acetate (and other esters) are obtained by conducting methyl ether and carbon monoxide over a catalyst (sodium formate or methoxide) heated under pressure at 300°–400° (Dreyfus, B.P. 319030, 1928).

Ethyl acetate is prepared by saturating a mixture of sulphuric acid and sodium acetate with ethylene. and distilling the diluted solution (Chem. Fabr. G.m.b.H. and Oehme, G.P. 372717).

For the production of amyl acetate from natural gasoline, the hydrocarbon fraction (mainly pentane) is chlorinated in contact with a catalyst, and the chlorinated product is esterified with sodium acetate in an autoclave (Koch and Burrell, Ind. Eng. Chem., 1927, **19**, 442).

Acetic Acid from Ethylidene Diacetate.—In the process claimed by Farbenf. vorm. F. Bayer & Co. (B.P. 360325, 1923) the diacetate is boiled with granulated zinc and the product is fractionally distilled.

Elimination of Mercury.—In the early years of the production of synthetic acid, mercury was almost invariably present as an impurity. To eliminate such traces of mercury the Chem. Fabr. Griesheim-Elektron and Grünstein boil the acid with a reactive organic material, such as cork or rubber, and redistil the acid after deposition of the mercury (G.P. 347190, 1915).

Properties of Acetic Acid.

Pure (glacial) acetic acid solidifies at 16·6° (Bousfield and Lowry, Chem. Soc. Proc. 1911, **27**, 187) in tabular or prismatic crystals. The glacial acid may be supercooled to −10° without solidification; on adding a crystal of acid the liquid solidifies and the temperature rises to 16·7°.

The crystals have d_4^{15} 1·0607 (Mendeléeff). When melted, they yield a colourless liquid d_4^{16} 1·0543 (Pettersson, J. pr. Chem. 1881 [ii], **24**, 301), d_4^{18} 1·05148, and d_4^{20} 1·04922 (Bousfield and Lowry, *l.c.*), and b.p. 118·5° at 760 mm. (Perkin), 118·1° (corr.) (Thorpe and Rodger). The vapour burns with a blue flame, producing water and carbon dioxide.

Glacial acetic acid is blackened when heated with conc. sulphuric acid, evolving sulphur dioxide and carbon dioxide. Nitric and chromic acids have no action. Chlorine, under the influence of sunlight, forms substituted chloroacetic acids.

The direct rays from a mercury vapour lamp decompose both acetaldehyde and acetic acid, the latter yielding carbon monoxide and other combustible gases and carbon dioxide (Berthelot and Gaudechon, Compt. rend. 1913, **156**, 68).

On adding water to glacial acetic acid heat is evolved; the density of the diluted acid rises to a maximum between 80 and 77%, and then falls; at 43% the density is the same as that of glacial acid (*see* table on p. 52). Oudemans' table of densities (Jahresber. Fortsch. Chem. 1886, 302) is used commercially as a rough means of ascertaining the strength of acetic acid by means of the hydrometer, especially in the vicinity of 30%. It is interesting to note that some 80% commercial acids do not correspond with the density given for that strength.

The following tables of the solidification points of mixtures of acetic acid and water are used in determining the strengths of acetic acid, especially those in the vicinity of glacial acid.

Solidifying point	Water to 100 parts pure acetic acid.	Solidifying point.	Water to 100 parts pure acetic acid.
°C.		°C.	
16·675	0	−3·94	16·38
16·50	0·05	−8·80	21·53
16·06	0·29	−12·80	24·56
14·54	1·15	18·10	29·97
11·81	2·94	−17·90	30·87
7·21	6·53	−23·87	36·57
2·95	10·33	−24·90	37·52
2·46	10·74	25·20	39·30
−2·90	15·80	−26·75	40

RÜDORFF'S TABLE OF SOLIDIFICATION POINTS OF MIXTURES OF ACETIC ACID AND WATER (Ber. 1870, **3**, 370).

100 parts of acetic acid mixed with water.	100 parts contain by weight.	Solidification point.
		°C.
0·0	0·0	+16·7
0·5	0·497	15·65
1·0	0·990	14·8
1·5	1·477	14·0
2·0	1·961	13·25
3·0	2·912	11·95
4·0	3·846	10·5
5·0	4·761	9·4
6·0	5·660	8·2
7·0	6·542	7·1
8·0	7·407	6·25
9·0	8·257	5·3
10·0	9·090	4·3
11·0	9·910	3·6
12·0	10·774	2·7
15·0	13·043	−0·2
18·0	15·324	2·6
21·0	17·355	5·1
24·0	19·354	7·4

Density of Aqueous Acetic Acid (Oudemans).

%	Density.		%	Density.		%	Density.	
	15°.	20°.		15°.	20°.		15°.	20°.
0	0·9992	0·9983	34	1·0459	1·0426	68	1·0725	1·0679
1	1·0007	0·9997	35	1·0470	1·0437	69	1·0729	1·0683
2	1·0022	1·0012	36	1·0481	1·0448	70	1·0733	1·0686
3	1·0037	1·0026	37	1·0492	1·0458	71	1·0737	1·0689
4	1·0052	1·0041	38	1·0502	1·0468	72	1·0740	1·0691
5	1·0067	1·0055	39	1·0513	1·0478	73	1·0742	1·0693
6	1·0083	1·0069	40	1·0523	1·0488	74	1·0744	1·0695
7	1·0098	1·0084	41	1·0533	1·0498	75	1·0746	1·0697
8	1·0113	1·0098	42	1·0543	1·0507	76	1·0747	1·0699
9	1·0127	1·0112	43	1·0552	1·0516	77	1·0748	1·0700
10	1·0142	1·0126	44	1·0562	1·0525	78	1·0748	1·0700
11	1·0157	1·0140	45	1·0571	1·0534	79	1·0748	1·0700
12	1·0171	1·0154	46	1·0580	1·0543	80	1·0748	1·0699
13	1·0185	1·0168	47	1·0589	1·0551	81	1·0747	1·0698
14	1·0200	1·0181	48	1·0598	1·0559	82	1·0746	1·0696
15	1·0214	1·0195	49	1·0607	1·0567	83	1·0744	1·0694
16	1·0228	1·0208	50	1·0615	1·0575	84	1·0742	1·0691
17	1·0242	1·0222	51	1·0623	1·0583	85	1·0739	1·0688
18	1·0256	1·0235	52	1·0631	1·0590	86	1·0736	1·0684
19	1·0270	1·0248	53	1·0638	1·0597	87	1·0731	1·0679
20	1·0284	1·0261	54	1·0646	1·0604	88	1·0726	1·0674
21	1·0298	1·0274	55	1·0653	1·0611	89	1·0720	1·0668
22	1·0311	1·0287	56	1·0660	1·0618	90	1·0713	1·0660
23	1·0324	1·0299	57	1·0666	1·0624	91	1·0705	1·0652
24	1·0337	1·0312	58	1·0673	1·0630	92	1·0696	1·0643
25	1·0350	1·0324	59	1·0679	1·0636	93	1·0686	1·0632
26	1·0363	1·0336	60	1·0685	1·0642	94	1·0674	1·0620
27	1·0375	1·0348	61	1·0691	1·0648	95	1·0660	1·0606
28	1·0388	1·0360	62	1·0697	1·0653	96	1·0644	1·0589
29	1·0400	1·0372	63	1·0702	1·0658	97	1·0625	1·0570
30	1·0412	1·0383	64	1·0707	1·0663	98	1·0604	1·0549
31	1·0424	1·0394	65	1·0712	1·0667	99	1·0580	1·0525
32	1·0436	1·0405	66	1·0717	1·0671	100	1·0553	1·0497
33	1·0447	1·0416	67	1·0721	1·0675			

Grimaux's Table of Solidification Points of Mixtures of Acetic Acid and Water (Compt. rend. 1873, **76**, 486).

Water.	Acetic acid.	Solidification point.
%	%	°C.
7·31	92·69	+ 5·3
13·25	86·75	− 1·4
23·52	76·48	−11·6
31·18	68·82	−19·3
33·56	66·44	−20·5
38·14	61·86	−24·0
44·50	55·50	−22·3
49·38	50·62	−19·8
56·54	43·46	−16·4
61·68	38·2	−14·8
69·23	30·77	−10·9
76·23	23·77	− 8·2
79·22	20·78	− 7·3
81·89	18·11	− 6·4
83·79	16·21	− 5·5

The break occurring in the curve of the solidification points at about 37% of water suggests the formation of a definite hydrate. Further evidence of the existence of distinct hydrates is afforded by the variations in longitudinal expansion and scattering of infra-red rays at different strengths (*cf.* Analyst, 1935, **60**, 454).

Richmond and England (Analyst, 1926, **51**, 283) published a table showing the relationship between the density, freezing-point and percentage composition of glacial acetic acid, as all likely impurities of the acid affect those properties.

Acetic acid forms normal, acid, and basic salts. It dissolves the oxides of certain metals, notably those of lead and copper, forming basic acetates. The action of dilute acetic acid upon aluminium is important, since aluminium cooking vessels are now so widely used. For a discussion of this question, *see* Burn (Analyst, 1932, **57**, 428) and Monier-Williams (Ministry of Health Rep. No. 78, 1935). Aluminium is attacked by boiling 90% acetic acid, an insoluble gelatinous basic acetate, $Al(O\cdot COCH_3)_2OH$, being formed, which probably acts as a protective coating on aluminium plant. The solubility of the metal increases with the dilution, 90% acid dissolving about ten times as much aluminium as 99%, and acid of lower strengths attacks the metal very rapidly. Slight variations in strength often have a pronounced influence on the solvent action (*cf.* Seligman and Williams, J.S.C.I. 1916, **35**, 88).

Block-tin, and gun-metal containing a sufficient proportion of tin, are the most suitable metals for acetic acid plant.

Acetic acid has a pungent odour and taste, and, when concentrated, produces blisters on contact with the skin. Glacial acetic acid is a bad conductor of electricity, but, on the addition of a little sulphuric acid, can be decomposed by an electric current, with the formation of carbon monoxide and dioxide and oxygen. Electrolytic decomposition of concentrated solutions of alkali acetates yields hydrogen and alkali at the negative, and ethane and carbon dioxide at the positive pole.

Acetic acid is miscible in all proportions with water, alcohol, ether, and chloroform. Resins, essential oils, fixed oils, etc., dissolve readily in the concentrated acid, and sulphur and phosphorus are sparingly soluble on heating.

The principal uses of acetic acid are : in the preparation of the acetates of lead, copper, iron, aluminium, etc. ; as pyroligneous acid in calico printing and the curing of hams, herrings, etc. ; as a solvent for resins, cellulose acetate, etc., in the preparation of varnishes, etc. ; in the preparation of artificial vinegar and for pickling vegetables ; in photography ; and in medicine as a local irritant, etc.

Analysis of Acetic Acid.

Commercial glacial acid should contain at least 98·9% of hydrogen acetate. The strength may be more accurately determined from the m.p. as given by Rüdorff (*l.c.*) than by titration.

Solidifying point.	16·70°	15·65°	14·80°	14·00°	13·25°	11·95°
Acetic acid %.	100	99·5	99·0	98·5	98·0	97·0

For more dilute acid the strength may be determined by titration with standard alkali, with phenolphthalein as indicator. For the titration of acid coloured with caramel (" vinegar essence ") the electrometric method (*cf.* Callan and Henderson, J.S.C.I. 1928, **47**, 329T) is more accurate than the use of a colour-indicator.

Small quantities of acetic acid may be detected by neutralising the liquid with potassium hydroxide, adding arsenious oxide, evaporating to dryness, and heating the residue, when the characteristic odour of cacodyl is emitted. The blue colour of " basic lanthanum acetate " with iodine is a highly sensitive test for acetates (Krüger and Tschirsch, Mikrochem. 1930, **8**, 337 ; *see also* page 55).

For the determination of acetic acid in acetates Pickell (Ind. Eng. Chem. 1920, **12**, 570) uses a method of distillation with xylene in the presence of phosphoric acid.

Impurities.—Commercial acetic acid may contain, as impurities, traces of sulphuric acid, sulphates, sulphurous acid, hydrochloric acid, chlorides, nitrates, arsenic (derived from sulphuric acid), copper, lead, zinc, iron and tin derived from the plant, and mercury from the synthetic process. For the detection of traces of such metals, *see* AERATED WATERS.

Formic acid is a common impurity of concentrated acetic acid, the amount varying from about 0·02 to 0·8%. Fincke's method of determining it is to boil the acid beneath a reflux condenser with sodium acetate and mercuric chloride and to separate and weigh the precipitated mercurous chloride (Z. Unters. Nahr. Genussm. 1911, **21**, 1, 88 ; Chem. Zentr. 1911, **1**, 1887 ; Analyst, 1911, **36**, 103, 455, 496).

Another method (Heermann, Chem.-Ztg. 1915, **39**, 124) is based upon the fact that formic acid will expel acetic acid from acetates. The acid is neutralised with sodium hydroxide and evaporated, and the residue is dried at 125° and weighed. It is then evaporated several times with formic acid and again dried at 125° and weighed, the difference in weight corresponding to the acetic acid expelled. The results for formic acid are about 0·02% too high, and those for acetic acid too low.

The presence of formic acid is indicated by the darkening which occurs at once when acetic acid is mixed with ammonia and heated with silver nitrate solution.

A method for the quantitative separation of *iso*valeric and acetic acids was devised by Chapman (Analyst, 1899, **24**, 114).

For the detection of *acetic anhydride* Klein (Ind. Eng. Chem. 1910, **2**, 389) described a test in which the acid was treated with selenious oxide or sodium selenite, a red precipitate of amorphous selenium being produced by the acetic anhydride, but not by pure glacial acetic acid. Another test (Edwards and Orton, Chem. Soc. Proc. 1911, **27**, 121) has been based upon the formation of insoluble anilides when acetic anhydride reacts with certain aniline derivatives, such as 2 : 4-dichloroaniline. These anilides may be separated and determined indirectly as chloroamine.

Aceto-acetic acid is detected by the violet colour obtained with sodium nitroprusside and ammonia, followed by acid in insufficient quantity to neutralise all the ammonia. Most commercial acetic acid, especially that produced by distillation from wood, contains traces of tarry substances. In the B.P. 1932 test for these and other oxidisable impurities, 5 ml. of the acid (33%) are diluted with 20 ml. of water and treated with 0·5 ml. of $N/10$ potassium permanganate solution. The pink colour should not disappear within half a minute.

In another test, to include both formic acid and other oxidisable impurities, 5 ml. of acid (33%) are treated with 2·5 ml. of $N/10$ potassium dichromate and 6 ml. of sulphuric acid, and after 1 minute 20 ml. of water are added and the mixture is cooled to 15° and then treated with 1 ml. of 10% potassium iodide solution, when a brown colour should be immediately produced. In applying the test to glacial acid the sample should first be diluted to twice its volume with water.

Methods for the analysis of synthetic acetic acid have been described by Reif (Z. Unters. Lebensm. 1924, **48**, 277), who found the following amounts of total aldehydes :—in crude acid, 0·46% ; technically pure, 0·02–0·05% ; chemically pure, 0·001–0·004%.

Acetates of Metals.

Aluminium Acetate.—The triacetate or normal acetate, $Al_2(C_2H_3O_2)_6$, does not appear to exist in the free condition. The solution technically known as *red liquor* (from its use in the production of red pigments and lakes, and in dyeing and calico printing) apparently contains a mixture of the diacetate and acetic acid. It is prepared by several methods.

Acetate of lime liquor is treated with the calculated amount of a solution of alum, and the mixture is agitated and allowed to settle from the deposited calcium sulphate. The supernatant liquid is concentrated to sp.gr. 1·087–1·10, and any further deposit of calcium sulphate is separated. Substitution of lead acetate for calcium acetate yields a better product, and aluminium sulphate may be advantageously used in place of the ordinary potassium or ammonium alum, the final red liquor containing more of the active alumina.

Red liquor usually contains the equivalent of 3 to 5% of alumina (Al_2O_3) and 6 to 10% of acetic acid ; its density varies from 1·085 to 1·120. Sodium carbonate is sometimes added to red liquor to neutralise the acidity.

An electrolytic method of making aluminium acetate has been claimed by Cruse (B.P. 213088, 1923).

Ammonium Acetate, $(NH_4)C_2H_3O_2$.—The crystalline salt is usually obtained by neutralising acetic acid with ammonia or by saturating the acid with dry gaseous ammonia. When evaporated, a solution of the salt loses ammonia and leaves a residue of acid acetate or diacetate. Pure ammonium acetate is completely volatile on heating. The official ammonium acetate of the B.P. is made by neutralising 33% acetic acid with ammonium carbonate.

Calcium Acetate, Diacetate of Lime, $Ca(C_2H_3O_2)_2,2H_2O$.—This salt is prepared by neutralising pyroligneous or acetic acid with lime or chalk, the *brown acetate of lime* being derived from pyroligneous and the *grey acetate* from the purer acid. The neutralised liquid is concentrated by evaporation, and the tarry impurities are skimmed from the surface. Much care is necessary in drying the salt to prevent decomposition, moisture being expelled by heating the mass first at 75° to 115° and finally at 125°. The brown acetate may be purified by dissolving it in hot water and filtering the solution through activated charcoal.

Acetate of lime is also made by conducting the vapours of *pyroligneous acid* into a cream of lime suspended in water and maintained at about 180° by adding quicklime (Chute, U.S.P. 939980, 1909). An apparatus for the continuous neutralisation with milk of lime of the vapours from the distillation of pyroligneous acid has been claimed (U.S.P. 1276043). A purer material may be obtained from commercial acetate of lime by boiling it with sodium hypochlorite and crystallising the clear supernatant liquid (Scott and Henderson, B.P. 6711, 1896). An analogous method of purification consists in treatment with an iron salt and a bleaching agent (Zinkeisen, U.S.P. 1213724, 1917).

Pure calcium acetate crystallises in needles or prisms containing 2 mols. of water. The crystals effloresce at the ordinary temperature and are completely dehydrated at 100°. The pure salt is readily soluble in water and in alcohol. The commercial salt usually contains from 1 to 8% of insoluble substances.

Calcium acetate is used in the preparation of acetic acid and of other acetates, and in calico printing.

Calcium acetate is usually evaluated by distillation with phosphoric acid and titration of the distillate (*see* Stillwell, J.S.C.I. 1904, **23**, 305 ; Grosvenor, *ibid.* 530 ; Gladding, Ind. Eng. Chem. 1909, **1**, 250). Formic acid may also be used to expel the acetic acid (*cf.* Heermann, *supra* ; " Allen's Organic Analysis," 5th ed., Vol. I., pp. 671 *et seq.*).

Copper Acetates, $Cu(C_2H_3O_2)_2,H_2O$.—The normal acetate is used in the manufacture of pigments. It is prepared by dissolving cupric oxide or verdigris in acetic acid.

Basic copper acetate. Verdigris. Vert-de-gris. Grünspan.—Verdigris is made at Grenoble and Montpellier by leaving copper plates immersed in a mass of *marcs* (skins and stems of grapes from wine factories) which have been allowed to undergo spontaneous acetic fermentation. When the copper is uniformly coated with verdigris it is removed and exposed to the air for two or three days, after which it is again returned to the fermenting mass, this procedure of exposure and immersion being alternately repeated until after about 6 to 8 weeks the plates have been completely eaten away. The verdigris is then kneaded into cakes in leather bags and dried. The product, termed *blue verdigris*, consists principally of the basic acetate, $(C_2H_3O_2)_2Cu_2O$.

Green verdigris, $CuO\cdot 2Cu(C_2H_3O_2)_2$, is made by arranging copper plates and cloths in alternate layers, which are moistened every few days for 5 or 6 weeks with pyroligneous or acetic acid, free access of air being allowed. In Abresh's process crystalline copper acetate is prepared directly from minerals containing the oxide or carbonate of copper (F.P. 391603, 1908).

The chief use of the various forms of verdigris is in the manufacture of oil and water colours, and of anti-fouling paints for ships' bottoms, etc. Verdigris is also used in dyeing and calico printing and in the manufacture of Schweinfurth green. When brass sheets have been used instead of copper, zinc will be present as an impurity. Clay, baryta, chalk, and sulphates of copper, barium and calcium are sometimes used as adulterants. A good sample of verdigris should yield about 3% of residue on solution in hydrochloric acid, with 6% as a maximum.

Aceto-Arsenite of Copper : Schweinfurth Green. *See* Arsenic.

Ferric Acetate, $Fe_2(C_2H_3O_2)_6$.—This salt, which is used as a mordant, is prepared by adding calcium or lead acetate to ferric sulphate or iron alum, care being taken to avoid excess of acetate.

Ferrous Acetate, $Fe(C_2H_3O_2)_2$. *Pyrolignite of iron. Iron liquid. Black liquor.*—This is prepared by treating iron turnings, nails, etc., with pyroligneous acid (sp.gr. 1·035 to 1·040), and skimming tarry substances from the surface as they rise. The resulting black liquid is concentrated to sp.gr. 1·120–1·140 by evaporation, the latter strength (known as *printer's iron liquor*) containing about 10% of iron. Dyers add copperas (ferrous sulphate) to the liquor to raise its density ; tannin is also sometimes added to form the black iron tannate.

Black liquor is also made by the interaction of ferrous sulphate and acetate of lime, the resulting product having sp.gr. 1·11.

To reduce the formation of ferric acetate by absorption of oxygen from the air, clean iron is frequently added to the finished liquor.

Black liquor is used in calico-printing and in dyeing, in the preparation of various dark colours and pigments, and for stains for leather, wood, etc.

Lanthanum Acetate, $La(C_2H_3O_2)_3,1\frac{1}{2}H_2O$ (*see* Lanthanum).—The basic lanthanum salt obtained on adding ammonia or sodium hydroxide to lanthanum chloride or nitrate gives intensely coloured iodo-compound in the presence of acetate or propionate ions and is applied as a sensitive reagent for acetate in the presence of a large excess of inorganic ions (Krüger and Tschirch, Ber. 1929, **62** [B], 2776).

Lead Acetate. *Normal or di-acetate of lead. Sugar of lead. Bleizucker.* $Pb(C_2H_3O_2)_2,3H_2O$.

White acetate of lead is made in leaden pans by the gradual introduction of litharge (16·5 parts) into 45% acetic acid (100 parts, or a corresponding amount of weaker acid), until the liquid is nearly neutral. It is then boiled, and, after removal of the scum of impurities, is evaporated to sp.gr. 1·5 and allowed to crystallise in another vessel. The mass of coarse crystals is drained on a rack and broken into lumps for sale. *Brown acetate* of lead is obtained in an analogous manner, but with the use of pyroligneous instead of acetic acid. As a rule, 2 parts of litharge produce about 3 parts of acetate.

In another process granulated lead, residues of white lead, etc., are placed in vessels arranged obliquely over one another. Strong acetic acid is introduced into the uppermost vessel and, after about 30 minutes, is allowed to run into the second vessel, and so on in succession until it reaches the lowest vessel. After removal of the acid the lead in the vessels absorbs oxygen rapidly from the air becoming hot. On leaving the last vessel the acid is again passed through the series, dissolving the acetate which has been formed, and after evaporation leaves crystals of the white acetate.

In Schmidt's process (B.P. 7192, 1897) the lead is placed in closed iron cylinders and exposed to the action of dilute acetic acid and oxygen.

Pure lead acetate is a white crystalline salt with a slightly sweet taste and weak acid reaction. It melts at 280°, and when heated more strongly forms a basic salt and suddenly solidifies. Its solubility in water is as follows : 54·35 parts in 100 at 25°, 87·77 parts at 35°, and 154·25 parts at 45°.

Lead acetate is used in dyeing and calico-printing, for the preparation of alum mordants, etc., in the manufacture of chrome yellow and other pigments, and in medicine.

Basic acetates of lead.—There are two well-defined basic acetates. The dibasic acetate, $Pb(C_2H_3O_2)_2PbO{\cdot}2H_2O$, is obtained by dissolving the calculated proportion of litharge in a solution of the normal acetate ; the tribasic acetate, $Pb(C_2H_3O_2)_2 2PbOaq.$, is prepared by boiling the normal acetate with excess of litharge.

Lead subacetate.—This salt, $CH_3{\cdot}CO_2Pb$, may be prepared by the interaction of acetic anhydride and lead suboxide at 195°. It is soluble in alcohol (*see* Denham, J.C.S. 1919, **115**, 109).

Solutions of lead subacetate are official drugs, dilute solutions being termed *Goulard water* or *Liquor plumbi subacetatis*, and strong solutions, *Goulard extract* or *Liquor plumbi fortis*.

Lead tetra-acetate, $Pb(C_2H_3O_2)_4$.—This salt, which is an efficient oxidising agent for converting the hydrogen ion into the hydroxyl group, is prepared from red lead and glacial acetic acid (Dimroth and Schweiger, Ber. 1923, **56** [B], 1377), or by the electrolysis of a solution of lead diacetate in acetic acid (Schall and Melzer, Z. Elektrochem. 1922, **48**, 47).

Complex acetates of lead and other metals.—Complex salts in which the lead acetate ion appears to act as a cation have been prepared by the action of perchloric or nitric acid on lead oxide and acetic acid, or on lead acetate under specified conditions. The perchlorate acetates explode violently when heated or struck (Weinland, Z. angew. Chem. 1921, **34**, 354 ; Weinland and Stroh, Ber. 1922, **55**, 2219). Other metals, *e.g.* sodium, strontium, barium, magnesium, can partly replace the lead in these complex salts (Weinland and Bauer, Ber. 1924, **57** [B], 1508). Other salts, such as dithionates, picrates, nitrates, and bromates, have been obtained by interaction with the acetato-perchlorates (Weinland and Paul, Z. anorg. Chem. 1923, **129**, 243 ; Weinland and Hinrichsen, Ber. 1923, **56** [B], 528).

Complex acetates containing calcium, strontium, barium, etc., have also been prepared by Dubský and Tesařík (Coll. Czech. Chem. Comm. 1929, **1**, 571), and analogous compounds containing copper, nickel, iron, manganese, zinc, cadmium, etc., have been described by Weinland and Holtmeier (Z. anorg. Chem. 1928, **173**, 49).

Magnesium Acetate.—A basic acetate of magnesium is prepared by heating the normal acetate with magnesia. In concentrated form it has been used as a disinfectant.

Potassium Acetate, $C_2H_3O_2K$, is a normal constituent of the juices of many plants. It is prepared by a process similar to that used for sodium acetate. It is a deliquescent crystalline salt, soluble in 0·53 part of water at 0°. A concentrated solution in hot water boils at 169°, and then contains 88% of the salt. A powerful, unstable bleaching liquid is obtained by passing chlorine into a solution of potassium acetate, carbon dioxide being evolved.

Sodium Acetate, $C_2H_3O_2Na,3H_2O$, is produced (1) by interaction of dilute acetic acid and sodium carbonate, and evaporation and crystallisation of the solution ; (2) by neutralisation of pyroligneous acid with soda, evaporation of the solution, and fusion of the salt to remove tarry substances ; (3) by the addition of sodium sulphate to a solution of calcium or lead acetate, decantation of the supernatant liquid, evaporation, and crystallisation.

Hydrated sodium acetate forms monoclinic crystals with a strongly saline taste ; it is soluble in 2·8 parts of cold water and in 0·5 part of boiling water. The crystals melt at 75° and lose their water of crystallisation at 100°. On dissolving this salt in strong acetic acid and rapidly evaporating the solution, the diacetate is obtained ; if glacial acetic acid is used, sodium triacetate is formed.

Sodium acetate is used in the manufacture of acetic acid and in medicine. It is liable to contain traces of sulphates, chlorides, and carbonates, and tarry substances when pyroligneous acid is used in its production.

Titanium Acetate.—A double acetate of titanium has been prepared by Kunheim (G.P. 248251) by adding excess of an alkali acetate solution to a strong solution of a tervalent titanium salt, and crystallising the double salt in a vessel from which air is excluded.

Anhydrous metallic acetates.—Anhydrous acetates of metals may be obtained by the interaction of the metallic nitrate containing water of crystallisation with acetic anhydride ; the anhydrous cupric, cuprous, cadmium, magnesium, cerium, manganic, ferric, cobalt, and chromic acetates are described (Späth, Monatsh. 1912, **33**, 235).

Alkyl Acetates.

Acetic acid forms numerous acetates with organic radicals, some being normal constituents of essential oils, others are technically important (B.S.S., 551, 552, 553, 1934).

Amyl Acetate.—Of the six isomeric amyl acetates, only *iso*amyl acetate, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O$, generally known as *amyl acetate*, is of technical importance. It is a colourless liquid with a pear-like odour, d_4^{15} 0·8762 (Mendeléeff), d_4^{22} 0·8562 (Brühl), b.p. 138·5°–139° at 758·6 mm. (Schiff).

It may be prepared by distilling a mixture of amyl alcohol (1 part), sulphuric acid (1 part), and dried potassium acetate (2 parts) ; also by heating a mixture of amyl alcohol (1), acetic acid (1), and sulphuric acid (0·5 part) on the water-bath, and pouring the solution into an excess of water. The upper layer is shaken with sodium carbonate solution, again separated, dried over calcium chloride and redistilled.

It is obtained commercially from fusel oil by a process involving the use of hydrochloric acid and calcium acetate (Wilson), and by the interaction of chloropentane and sodium acetate in the presence of strong acetic acid.

A continuous process (U.S.P. 1433308) consists in passing a mixture of amyl alcohol and ethyl acetate, with a little sulphuric acid, through a heated rectifying column, from which the amyl acetate (of higher b.p.) is continuously drawn off.

Amyl acetate is insoluble in water, but dissolves readily in ether, amyl alcohol, and ethyl alcohol. A dilute solution in spirit is used for flavouring confectionery.

It is a good solvent for camphor, tannin, resins, cellulose nitrate, etc., and is used in cellulose paints and lacquer varnishes. It is also largely employed in the manufacture of photographic films, in some smokeless powders, and as an illuminant in the Hefner lamp.

Butyl Acetate, $C_2H_3O{\cdot}OC_4H_9$.—The following isomers of butyl acetate have been prepared : (1) *n*-butyl acetate, b.p. 124·4° (Linnemann) ; (2) *sec.*-butyl acetate, b.p. 111°–113° (de Luynes) ; (3) *iso*butyl acetate, b.p. 116° (Richards, Matthews) ; (4) *tert.*-butyl acetate, b.p. 96° (Butlerow). Both the normal and *iso*-acetates are commercial products, one of their chief uses being as substitutes for amyl acetate as solvents for cellulose nitrate in lacquers, etc.

The normal ester is prepared by slowly adding sulphuric acid to *n*-butyl alcohol, introducing the mixture into another vessel containing calcium acetate in slight excess, mixing the contents at 100°, and separating the butyl acetate by distillation with steam. The reaction is promoted by the use of acetic acid and butyl alcohol as catalysts. As sold, the esters contain about 85% of butyl acetate.

Ethyl Acetate.—*Acetic ether*,

$$C_2H_3O{\cdot}OEt,$$

is a clear colourless liquid, d_4^0 0·9245 (Wade and Merriman), d_4^0 0·92446 (Young and Forty) ; b.p. 77·17° at 760 mm. (Young and Forty) ; freezing-point −83·6° (Zimmermanns, van der Horst, and Kamerlingh Onnes, Compt. rend. 1922, **174**, 365).

Ethyl acetate may be prepared by treating absolute alcohol (3·6 parts) with sulphuric acid (9 parts), and after 24 hours pouring the mixture on fused sodium acetate (6 parts). After a further 12 hours the ethyl acetate is distilled off, dried over calcium chloride and potassium carbonate, and redistilled.

A commercial process claimed by Consort. f. Elektrochem. Ind. G.m.b.H. (B.P. 4887, 1915) consists in causing aluminium ethoxide to act upon acetaldehyde in the presence of aluminium chloride, preferably added during the preparation of the ethoxide from aluminium and alcohol ; the catalytic action may be intensified by melting the ethoxide and dissolving it in anhydrous camphor, alum, etc.

In another process, claimed by Farbw. vorm. Meister, Lucius, & Brüning (B.P. 1288, 1915), a solution of aluminium ethoxide in an organic solvent, such as xylene, is made to act at 0°–15° on acetaldehyde, a yield of about 86% of the theoretical amount of ethyl acetate being obtained (*cf.* Senderens and Aboulenc, Compt. rend. 1911, **152**, 1671).

For a method of preparing ethyl acetate from the ethylene in industrial gases, *see* G.P. 372717, according to which the ethylene is absorbed by a mixture of sulphuric acid and sodium acetate, water being then added, and the resulting ethyl acetate distilled under reduced pressure and purified by redistillation, etc.

The solubility of water in ethyl acetate is about 1 part in 8 at 0° and less at 15°, whilst water dissolves 26 parts of ethyl acetate at 0° and 24 parts at 15°.

The *acetic ether* of commerce is a mixture of ethyl acetate (about 75%) with other substances such as acetic acid, alcohol, ether, water.

Methyl Acetate, $C_2H_3O{\cdot}OMe$, is normally present in small quantity in wood spirit and in artificial vinegar made from wood acid. It is a colourless liquid with a fragrant aroma; d_{15}^{15} 0·9398; b.p. 57·5° at 760 mm. (Perkin). Soluble in water, alcohol, and ether. It may be obtained by distilling a mixture of methyl alcohol (1 part), potassium acetate (1 part), and sulphuric acid (2 parts), the distillate being dried over calcium chloride and lime and redistilled. Methyl acetate is used as a solvent for resins, cellulose nitrate, etc.

Propyl Acetates, $C_2H_3O{\cdot}OC_3H_7$.—*n*-Propyl acetate boils at 101·6° (Young and Thomas) and the *iso*-compound at 90°–93° (Friedel).

*iso*Propyl acetate, which forms a constituent of solvent mixtures for dissolving nitrocelluloses, may be obtained by the process described by Arnold (B.P. 300418, 1927), according to which *iso*propyl alcohol and acetic acid are made to interact by means of a catalyst, *e.g.* 0·2 to 3% of sulphuric acid.

Acetic Anhydride and Acetamide.

Acetic anhydride, $(CH_3{\cdot}CO)_2O$, is readily formed by heating acetyl chloride with a metallic acetate. The method originally used by Gerhardt (Ann. Chim. Phys. 1853 [iii], **37**, 285) consisted in treating anhydrous potassium or sodium acetate with a chloride or oxychloride of phosphorus (*cf.* Geuther, Annalen, 1862, **123**, 114). The commercial demand for acetic anhydride has led to the replacement of the expensive phosphorus chloride by an anhydrous chloride or oxychloride of sulphur. For a study of the reactions that take place when organic acids are treated with sulphur monochloride, *see* Denham and Woodhouse, J.C.S. 1909, **96**, 1235; 1913, **103**, 1861.

Sulphur chloride processes.—Kessler (F.P. 315938, 1901) used the process depending upon the action of sulphur chloride on anhydrous sodium acetate, but claimed that by distilling off the acetic anhydride under reduced pressure the production of sulphur dioxide is prevented. This practice has been adopted in many later methods. Dreyfus (B.P. 100450, 1916) has described the conditions to be followed to avoid the formation of sulphur dioxide and chloroacetic acids. They comprise: (1) the use of the reacting substances in the proportion of 6 atoms of chloride to 8 of sodium acetate; (ii) the presence of a diluent to prevent the effect of local excess of sulphur chloride and of overheating; (iii) gradual addition of the chloride and prevention of the temperature rising above 15° during the addition. The equations representing the respective reactions with sulphur monochloride and dichloride are as follows:—

$$8CH_3.COONa+3S_2Cl_2=4(CH_3{\cdot}CO)_2O+6NaCl+Na_2SO_4+5S$$

$$8CH_3{\cdot}COONa+3SCl_2=4(CH_3{\cdot}CO)_2O+6NaCl+Na_2SO_4+2S$$

To reduce the loss of sulphur it is thus advisable to use the sulphur chloride containing the higher proportion of chlorine. In the process claimed by the A.-G. für Anilin-Fabr. (G.P. 273101; J.S.C.I. 1914, **33**, 667) all loss of sulphur is eliminated by passing chlorine into a mixture of sodium acetate and sulphur chloride kept below 20°, thus

$$8CH_3{\cdot}COONa+SCl_2+2Cl_2=4(CH_3{\cdot}CO)_2O+6NaCl+Na_2SO_4$$

This patent is similar to that of Goldschmidt (B.P. 25433, 1908) according to which the whole of the sulphur chloride is generated *in situ* by the interaction of 6 atoms of chlorine and 1 atom of sulphur at a low temperature in presence of 8 to 9 mols. of sodium acetate. The sulphur may be replaced by a metallic compound containing sulphur (*e.g.* ferrous sulphide) (addition to F.P. 408065, 1910), and it was subsequently found (addition to same patent) that the reaction may be carried out at 40° to 50°. In de Jahn's process (B.P. 5039, 1910) claim is made for the use of several oxidisable compounds of sulphur.

Strosacker (U.S.P. 1403920, 1922) claims a process in which a mixture of sulphur chloride and sodium acetate is maintained under pressure at 20°, the temperature being then gradually raised to distil the acetic anhydride. The impure product is treated with manganese dioxide to remove sulphur compounds and then redistilled.

In Wacker's process (B.P. 211167, 1924) chlorine is led under pressure into a mixture of glacial acetic acid and sulphur chloride, and, after expulsion of sulphur dioxide and hydrogen chloride by heat, the residue is fractionated to obtain the acetic anhydride.

The conditions for obtaining the maximum yield of acetic anhydride from sodium acetate and sulphur monochloride in the presence of powdered antimony as catalyst have been studied by Mashino (J. Soc. Chem. Ind. Japan, 1921, **24**, 1023). Sulphur dioxide is removed from the product by distillation, chlorine by means of sodium acetate, and sulphur by means of phosphoric anhydride.

Capelli (Giorn. Chim. Ind. Appl. 1921, **3**, 356) has described a method of obtaining acetic anhydride free from secondary products. Sulphur monochloride which has absorbed 50% of chlorine at −14° is used as the reagent, and is claimed to give a yield of 76% of pure anhydride.

Use of oxychlorides of sulphur.—Several processes have been based on the reaction of sulphuryl chloride with sodium acetate:

$$4CH_3{\cdot}COONa+SO_2Cl_2=2(CH_3{\cdot}CO)_2O+2NaCl+Na_2SO_4$$

Thus, Farbenf. vorm. Bayer & Co. (B.P. 21560, 1900) treat dry sodium acetate with a mixture of chlorine and sulphur dioxide (the latter in excess) at 20° in a closed vessel. Sulphur dioxide forms an addition compound with sodium acetate, and this is decomposed by chlorine, yielding acetyl chloride or acetic anhydride according to the proportion of sodium acetate present. If necessary, the reaction may be controlled by mixing the addition compound with sand or an anhydrous inorganic salt (Farbw. vorm. Meister, Lucius & Brüning, G.P. 210805, 1907). Sulphuryl chloride may be made by mixing liquid sulphur dioxide and chlorine in a special vessel in presence of a catalyst, such as camphor or glacial acetic acid (B.P. 24255, 1902). In the process claimed by the A.-G. für Anilin-Fabr. (G.P. 226218, 1909) acetic anhydride is used as the catalyst for the preparation of sulphuryl chloride, the reaction products being separated by fractional distillation. It is not essential, however, to separate the sulphuryl chloride, and the same patentees use acetic anhydride both as an absorbent for the two gases and as a diluent in the subsequent reaction with sodium acetate (B.P. 23924, 1910).

Use of inorganic anhydrides.—A method involving the direct use of sulphuric anhydride was claimed by Fabr. van Chem. Prod. Schiedam (B.P. 12130 and 12042, 1913). An addition compound of glacial acetic acid with sulphuric anhydride is made to react at a low temperature with sodium acetate, but the resulting anhydride is only of low strength. In the process of Dreyfus (B.P. 17920, 1915) a solid addition compound of sulphuric anhydride and sodium sulphate is prepared, and this is subsequently made to react with sodium acetate suspended in acetic anhydride, the reaction being finally completed at 60°–70°. In a later patent (U.S.P. 1338979, 1920) Dreyfus claims the use of a process in which sulphuric anhydride is made to react at a low temperature with a dry acetate. To this class also belongs the process of Dreyfus (U.S.P. 1430304, 1926) in which the acetate is treated with a pyrosulphate.

Ruzicka's process (B.P. 283781, 1927) consists in conducting sulphur trioxide fumes into glacial acetic acid, and in a process claimed by U.S. Industr. Alcohol Co. (B.P. 353381, 1931) liquid sulphur dioxide is the reagent. Sulphur dioxide is used in a process described by Dreyfus (B.P. 305147, 1927), according to which a mixture of acetic acid vapour with 5 to 10% of sulphur dioxide is passed through packed tubes at 450°–600°, the water being subsequently removed by means of sodium bisulphate at 150°–200°. The Chem. Fabr. von F. Heyden (G.P. 358774, 1914) uses a cold solution of sulphuric anhydride in sulphuryl chloride as the reagent. This process belongs to the group in which the sulphuric anhydride is used in association with chlorine compounds. Thus, the Badische Co. (B.P. 24255, 1902) uses as the reagent sodium chlorosulphonate (obtained by the action of chlorosulphonic acid on sodium chloride), the reaction with sodium acetate being

$$NaSO_3Cl + 2CH_3\cdot COONa = (CH_3\cdot CO)_2O + NaCl + Na_2SO_4$$

A similar process is claimed by Dreyfus (B.P. 17920, 1915), who uses a compound formed by the direct absorption of sulphuric anhydride by sodium chloride. This compound (pyrosulphuryl chloride, $ClSO_2\cdot O\cdot SO_2Cl$) is also formed, together with carbonyl chloride, by the interaction of sulphuric anhydride and carbon tetrachloride, and will react with sodium acetate to form acetic anhydride (Beatty, B.P. 18823, 1912).

Use of carbonyl chloride.—A continuous process of obtaining acetic anhydride has been based by Leach and United Alkali Co. (B.P. 137701, 1919) on the interaction of sodium acetate and carbonyl chloride :

$$2CH_3\cdot CO_2Na + COCl_2 = (CH_3\cdot CO)_2O + CO_2 + 2NaCl$$

Another process is that of Imray (B.P. 328572, 1929), according to which concentrated acetic acid is treated with carbonyl chloride in presence of 10% of aluminium chloride, magnesium acetate, or an oxide, chloride, or acetate of a metal of Group I or II.

Synthesis from acetylene.—Some of the earliest synthetic methods of making acetic anhydride were based on the hydration of acetylene to aldehyde in presence of a mercury salt as catalyst, with the production of ethylidene diacetate, which on distillation yields acetic anhydride (B.P. 23190, 1914 ; 110906, 1917 ; 112765, 1917). In another process (Mathewson and Grattan, U.S.P. 1425500, 1922) acetylene is conducted through concentrated acetic acid (96–100%) in presence of a finely divided mercury salt.

In the process claimed by Elektrizitäts A.-G., Vienna (B.P. 23190, 1915), ethylidene diacetate is heated above its b.p. (169°) in presence of a catalyst, and in the process claimed by Consort. f. Elektrochem. Ind. G.m.b.H. (G.P. 391674, 1921) a solid carrier in a fine state of division is saturated with sulphuric or hydrochloric acid and heated with ethylidene diacetate.

In another process (Soc. des Usines Rhône-Poulenc, B.P. 318960, 1929) the vapours from crude ethylidene diacetate are passed through a suspension containing organic salts (*e.g.* potassium acetate), into a mixture of ethylidene diacetate and acetic acid (*see* page 38).

Catalytic "dehydration."—"Dehydration" of acetic acid vapour by the action of a catalyst forms the basis of several processes. In one of these (B.P. 280972, 1926) the vapour is passed over heated phosphoric acid, and the acetic anhydride is separated by fractional distillation ; or the vaporised catalyst (preferably phosphoric acid) is entrained with the acetic acid vapour at 600° (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 279070, 1927). In another process claimed by the same patentees (G.P. 442256, 1925) the acetic acid vapour is heated in containers of graphitic or calcined carbon, in presence of a catalyst such as a fused phosphate.

Dreyfus (B.P. 305147, 1927) "dehydrates" the acetic acid by passing a mixture of the acid vapour and hydrogen through a copper tube at 500°–700° ; and Berl (B.P. 344482, 1929) passed vaporised acetic acid over a copper or silver catalyst on tungstic acid, asbestos, pumice, etc., the process being promoted by admission of air. In other patents (B.P. 336668 and 336960, 1929) Dreyfus claims the use of asbestos as a carrier, and of oxides of arsenic or antimony as catalysts. It is also claimed that a silica gel, with or without the addition of other catalysts, will effect the "dehydration" at 550°–650°. The vapours issuing from the apparatus are washed with benzene to extract the acetic anhydride (Brit. Celanese, Ltd., Oxley and Fallow, B.P. 340484, 1929). The catalyst claimed as a "dehydrating" process in B.P. 314555, 1928, is tungstic acid or a tungstate.

Pyrogenic decomposition and extraction.—The process claimed by Brit. Celanese, Ltd., Dreyfus and Haney (B.P. 298667, 1927) is based on the decomposition of acetic acid at 600°–1000°, and the acetic anhydride is extracted from the pyrogenic vapours by means of a mixture of light petroleum and ether.

For the separation of acetic anhydride from its admixture with acetic acid and water, Stevens (B.P. 379042, 1931) adds brine and uses benzene or other suitable solvent for the extraction. Another extraction process is claimed by Boehringer & Soehne G.m.b.H. (B.P. 372434, 1931).

Synthesis from acetone and carbon monoxide.—A process for the manufacture of acetic anhydride directly from acetone and carbon dioxide is claimed by Brit. Celanese, Ltd., and Bader (B.P. 237302, 1924).

From ethyl alcohol.—In a process claimed by Dreyfus (B.P. 338518–9) a mixture of the vapour of alcohol with air or air and steam is conducted over a catalyst, such as an alkaline earth oxide, at 430°–480°.

PROPERTIES.—Pure acetic anhydride boils at 139·5° at 760 mm. and has d_4^{15} 1·0876, d_4^{20} 1·0820 (Orton and Jones, J.C.S. 1912, **101**, 1720). The commercial product, which usually contains a little acetic acid, boils at about 138°. Specific heat 0·434, and latent heat of vaporisation 66·1 cals. per kg. (Berthelot); n_D^{20} 1·39038 (Landolt).

Acetic anhydride is not immediately converted into acetic acid on contact with cold water, but above 20° the hydration proceeds rapidly. When treated with concentrated sulphuric acid at 0° it forms an addition compound, acetylsulphuric acid, changing with rise of temperature into the isomeric sulphoacetic acid, $HSO_3{\cdot}CH_2{\cdot}COOH$ (*see* Stillich, Ber. 1905, **38**, 1241). It also combines with nitric, boric, and formic acids. Formyl acetic acid combines with alcohols to produce esters and gives formyl derivatives with amines.

The commercial uses of acetic anhydride include the manufacture of cellulose acetate, acetylsalicylic acid, and diacetylmorphine (heroin); it is also used in the dyestuffs and pharmaceutical industries, and is a valuable laboratory reagent for the determination of the "acetyl value" of hydroxylated fats, etc.

ANALYSIS.—The commercial product should contain not more than traces of phosphorus, sulphur chlorides, chloro-acetic acid, and higher homologues. It should also be free from metals, notably copper and mercury.

In determining the strength of acetic anhydride by titration it is preferable not to boil the sample beneath a reflux condenser (Perf. and Essent. Oil Rec. 1922, **13**, 172), since this sometimes makes the indicator insensitive. It is better to hydrolyse the anhydride in the cold with a measured excess of standard sodium hydroxide solution, to add a known quantity of $N/2$ acid, and to titrate with $N/2$ alkali.

Richmond and Eggleston (Analyst, 1926, **51**, 281) found Menschutkin's and Wassilieff's method (based on the formation of acetanilide from aniline) to be accurate but tedious (*see* Radcliffe and Medofski, J.S.C.I. 1917, **36**, 628). They recommended a thermometric method, in which the heat evolved on treating acetic anhydride (diluted with toluene) with aniline is measured; the results were more accurate than those obtained by direct titration. An analogous thermometric process has been devised by Somiya (Proc. Imp. Acad. Tokyo, 1927, **3**, 79; 1927, 439), a 25% solution of aniline in acetic acid being used as the reagent.

The ordinary rules for the critical temperatures of solution are not applicable to mixtures of acetic acid and acetic anhydride (*see* Crismer and Tommerman, Bull. Soc. chim. Belg. 1920, **29**, 46).

In a method devised by Calcott, English, and Wilbur (Ind. Eng. Chem. 1925, **17**, 942) acetic anhydride is determined by dissolving it in glacial acetic acid, adding excess of 2 : 4-dichloroaniline, and titrating the excess with standard sodium nitrite solution.

Whitford (J. Amer. Chem. Soc. 1925, **47**, 2939) has based a quantitative method on the measurement of the oxides of carbon evolved when a solution of acetic anhydride in pyridine is treated with oxalic acid. The reagents and the water over which the gas is collected are previously saturated with carbon monoxide and dioxide. A volumetric application of this reaction has been devised by Rosenbaum and Walton (*ibid.* 1930, **52**, 3566), the excess of oxalic acid being titrated with standard permanganate solution.

For the determination of propionic acid in acetic anhydride, Baum (Chem.-Ztg. 1927, **51**, 517, 528) has devised a method in which the anhydride is converted into acetate, the solution then oxidised with potassium dichromate and sulphuric acid, and the amount of propionic acid calculated from the quantity of dichromate reduced.

ACETAMIDE, $CH_3{\cdot}CO{\cdot}NH_2$.— Acetamide is obtained by dry distillation of (i) ammonium acetate, and (ii) ammonium diacetate, the latter yielding a pure product (91·7%). Acetamide begins to distil at 195°–222°, and at 222° the distillation is stopped, the residue then consisting of pure acetamide (*see* François, J. Pharm. Chim. 1906 [vi], **23**, 230).

Another method of obtaining a pure product is to saturate a mixture of ethyl acetate and ammonia with dry ammonia gas at −10°, and to submit the products of the reaction to fractional distillation *in vacuo*.

A synthetic method of preparing acetamide (and acetic acid) from formamide or from carbon monoxide and ammonia is claimed by the Soc. Franç. de Catalyse Généralisée (B.P. 371555, 1931). Formamide vapour and hydrogen, with or without steam, are passed into a tube heated at 250°–300° and containing a catalyst, *e.g.* copper powder and alumina, and subsequently exposed to ultra-violet radiation.

Properties.—Acetamide forms white, odourless, hexagonal crystals, m.p. 81°–82°, b.p. 222° (corr.). It dissolves readily in water, and when heated with alkali or acid is converted into acetic acid and ammonia. It acts both as a base and an acid, combining with hydrogen chloride or nitric acid, and forming compounds in which one atom of hydrogen is replaced by a metal, *e.g.* $C_2H_3O{\cdot}NHAg$. Forster (J.C.S. 1898, **73**, 783) found that mercury acetamide is an active dehydrogenating agent, and therefore a convenient reagent for the detection of primary and secondary hydrazines and primary hydroxylamines.

When chlorine is conducted into fused acetamide, acetochloroamide, $CH_3{\cdot}CONHCl$, is produced. The analogous bromine compound is converted into methylamine when distilled with a strong aqueous solution of sodium hydroxide (Hofmann, Ber. 1882, **15**, 765).

Acetamide readily forms addition compounds (*see* Morgan, Chem. Soc. Proc. 1906, **23**), such as molecular compounds of the type $CH_3{\cdot}CONH_2{\cdot}X$, where X represents an organic or inorganic acid or an inorganic salt. With formaldehyde, paraformaldehyde, or trihydroxymethylene it gives condensation products of the type $CH_3{\cdot}CONH{\cdot}CH_2{\cdot}OH$. These have found a commercial use as antiseptic agents and as solvents for uric acid (G.P. 164610, 1902).

Diacetamide, $NH(C_2H_3O)_2$, and its derivatives (*see* Hofmann, Ber. 1890, **23**, 2394 ; Curtius, *ibid.* 3037 ; König, J. pr. Chem. 1904 [ii], **69**, 1 ; Tröger, *ibid.* 347).

Triacetamide, $N(C_2H_3O)_3$, and its derivatives (*see* Wichelhaus, Ber. 1870, **3**, 847).

C. A. M.

ACETIN. *Acetine.* The acetins are the acetyl esters of glycerol, or glyceryl acetates. Theoretically, five of these can exist—namely, two mono-, two di-, and one tri-derivative, according to the number and position of the acetyl groups attached to the glyceryl radicle—but so far only four of these have been obtained in an approximately pure state.

Geitel (J. pr. Chem. 1897 [ii], **55**, 417) showed that by heating glycerol with an excess of glacial acetic acid or acetic anhydride, mixtures of triacetin with di- and monoacetin were obtained : the proportion of triacetin in the product was greater, the higher the temperature and the greater the proportion of acetic acid employed. Triacetin was separated by extracting an aqueous solution of the mixed product with ether. Diacetin and monoacetin were recovered by fractional distillation and further extraction of the residual solution : acetylated condensation products of glycerol, such as monoacetyldiglycerol, diacetyldiglycide, triacetyldiglycerol, etc., may also be present in the crude reaction product.

Triacetin is a colourless liquid, having d^{15} 1·1605 (Geitel), d^{25}_4 1·1562 (Jaeger, Z. anorg. Chem. 1917, **101**, 70), and b.p. 172°–172·5°/40 mm. (Geitel) ; b.p. 260°/760 mm. (Jaeger) ; it dissolves in water to the extent of about 7% at 5°, and is miscible in all proportions with alcohol, ether, chloroform, and benzene.

Diacetin, b.p. 175°–176°/40 mm., d^{15}_{15} 1·1779 (Geitel), b.p. 155°–156°/15 mm. (Wahl, Bull. Soc. chim. 1925, **37**, 713), as prepared by Geitel's method, or by similar laboratory or commercial processes (*cf.* Wahl, *l.c.*, Esselen and A. D. Little, U.S.P. 1509864), consists chiefly, if not entirely, of the $\alpha\gamma$-glyceryl diacetate $OH{\cdot}CH(CH_2{\cdot}OAc)_2$, b.p. 149°/12 mm. (Wegscheider and Zmerlikar, Monatsh. 1913, **34**, 1061). The presence of small proportions of $\alpha\beta$-diacetin in ordinary preparations of diacetin is possible, although not conclusively proved. (The method employed by Wegscheider and Zmerlikar (*l.c.*) for the attempted synthesis of this isomer is now known to be unreliable, and the diacetin, b.p. 140°–142°/1·2 mm. prepared by these workers can have been at best a mixture of the $\alpha\beta$ and $\alpha\gamma$ isomerides.) Diacetin is readily soluble in water and alcohol, but is only difficultly soluble in ether or benzene when water is present.

Similarly, *mono-acetin*, b.p. 130°–132°/2–3 mm., d^{15}_{15} 1·2212 (Geitel), d^{25}_4 1·1984, n^{25}_D 1·4481 (Schuette and Sah, J. Amer. Chem. Soc. 1926, **48**, 3161), prepared by Geitel, or by heating molecular equivalents of glycerol and acetic acid in the presence of phosphoric acid or phosphorus pentoxide (Schuette and Sah), or by heating triacetin with glycerol, consists chiefly or entirely of α-glyceryl acetate,

$$CH_2(OAc){\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

b.p. 103°/0·4 mm. (Fischer and Pfähler, Ber. 1920, **53** [B], 1612 : monoacetin suffers more or less decomposition when distilled at higher pressures and temperatures). Monoacetin is very soluble in water, and is not precipitated from a concentrated aqueous solution by the addition of salt (distinction from diacetin) : it is readily soluble in chloroform (distinction from glycerol), but is not very soluble in ether or light petroleum. Authentic β-glyceryl acetate, $CH_2(OH){\cdot}CH(OAc){\cdot}CH_2(OH)$, b.p. 117°–118°/0·3 mm., has been synthesised by Bergmann and Carter (Z. Physiol. Chem. 1930, **191**, 211).

Commercial triacetin (" *Acetine* ") is manufactured by acetylating glycerin with a large excess of glacial acetic acid and distilling off the surplus acid ; occasionally, esterification catalysts such as potassium hydrogen sulphate, zinc chloride, or sodium acetate (Sonn, B.P. 425611) are employed. It is a water-white, syrupy liquid having d^{15} about 1·168, b.p. 260°/760 mm. and an acetyl content of about 80–81% (as acetic acid), which corresponds to a mixture of 90% of triacetin with 10% of diacetin. The commercial value of triacetin is assessed from determinations of the specific gravity and free and combined acetic acid : the British Standards Specification 2 D 11 (Acetin) requires a colourless product, free from glycerol, mineral acid and salts, having $d^{15} \nless 1{\cdot}16$ and $\ngtr 1{\cdot}17$, an acetyl content (calculated as acetic acid) of $\nless$ 80% by wt., an acidity $\ngtr$ 0·15% by wt. (calculated as acetic acid), and ash $\ngtr$ 0·02%.

When mixed with twice its volume of benzene, the acetin shall remain clear on cooling to 0°C. (test for absence of water and glycerol). The specification prescribes that the free acidity shall be determined by titrating a mixture of 25 c.c. of acetin and 50 c.c. of distilled water with *N*/2 ammonia, litmus being employed as indicator. The acetyl content is determined by saponifying 0·5 g. of the sample with 20 c.c. of *N*/1 caustic soda on the steam bath (1 hr.) and titrating back the excess alkali with *N*/1 sulphuric acid.

Triacetin is employed as a plasticiser for acetyl-cellulose lacquers, and to a lesser extent in nitro-cellulose and ethyl-cellulose compositions : it may be added in any proportion without causing cloudiness, but the films obtained tend to be too soft if the amount of triacetin is large. Triacetin is a partial solvent for ester gums, shellac, copals, etc., and can be usefully employed in lacquers embodying such resins or glyceryl phthalate resins. Triacetin is also employed in essence manufacture to render various essential oils more soluble, and is a valuable solvent for induline and other basic colouring matters employed by the calico printer as steam colours.

Commercial *diacetin*, d^{15} about 1·18, b.p. 259°/760 mm., is used to a limited extent for similar purposes : it dissolves cellulose acetate and nitrate, shellac, glyceryl phthalate resins, etc., but does not dissolve ester gums or copals.

Monoacetin is one of the usual solvents for basic dyes employed in printing paper-bags.

E. L.

ACETOACETANILIDE,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5,$$

m.p. 85°. Intermediate product for the manufacture of dyes.

ACETOACETIC ACID,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$$

The free acid is a thick colourless liquid with a strongly acidic reaction ; it is miscible with water in all proportions. On heating it decomposes somewhat violently at about 100° into acetone and carbon dioxide :

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH \rightarrow CO_2 + CH_3{\cdot}CO{\cdot}CH_3$$

On treatment with barium carbonate it gives an amorphous barium salt,

$$(CH_3{\cdot}CO{\cdot}CH_2{\cdot}COO)_2Ba,H_2O$$

(Ceresole, Ber. 1882, **15**, 1327, 1872); the silver and copper salts are less stable than the barium salt. With ferric chloride it gives a violet coloration.

The free acid may be prepared from its ethyl ester by treating the latter with a slight excess of 2½% aqueous potassium hydroxide, allowing to stand in the cold for 24 hours, acidifying with sulphuric acid, and extracting with ether. It may be purified by treating the crude material obtained from the ether extract with barium carbonate, and extracting unchanged ester with ether. The barium salt is then decomposed with sulphuric acid and the acetoacetic acid extracted with ether (Ceresole, *l.c.*).

Acetoacetic acid 2 : 4-dinitrophenylhydrazone has m.p. 125° (Clift and Cook, Biochem. J. 1932, **26**, 1800).

The kinetics of the ketonic decomposition of acetoacetic acid have been studied by Widmark (Acta med. Scandinav. 1920, **53**, 393 ; A. 1921, **120**, ii, 183). Euler and Ölander (Z. anorg. Chem. 1925, **147**, 304) have measured the velocity of the catalytic decomposition in solutions of p_H 11 to p_H 15·07 at 37°. The velocity of the reaction I

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH \rightarrow CH_3{\cdot}CO{\cdot}CH_3 + CO_2$$

becomes zero at $p_H = 14{\cdot}19$; while that of the reaction II

$$CH_3{\cdot}C(ONa){:}CH{\cdot}COONa + H_2O \rightarrow 2CH_3{\cdot}COONa$$

becomes 130×10^{-5} at $p_H = 15{\cdot}07$.

	I.	II.
p_H	$k \times 10^{-5}$	$k \times 10^{-5}$
11·11	3·01	0
13·21	3·37	0
13·60	1·98	0·80
13·90	1·52	2·18
14·19	0	19·6
15·07	0	130

Acetoacetic acid appears in the urine of diabetic patients. The detection and estimation of this acid in urine have been the subject of much controversy. Arnold (Wiener Klin. Woch. **12**, 541 ; Centr. inn. Med. **21**, 417, *see* A. 1900, **78**, ii, 113, 768 ; Chem. Zentr. 1899, **70**, ii, 146 ; 1900, **71**, ii, 345) makes use of diazoacetophenone as a test for acetoacetic acid. Riegler (Bull. Soc. Sci. Bucarest, **11**, 290, *see* A. 1903, **84**, ii, 112 ; Chem. Zentr. 1902, **73**, ii, 846) uses the red colour produced by the addition of sulphuric and iodic acids. Bondi (Wiener Klin. Woch. **19**, 37, *see* A. 1906, **90**, ii, 588 ; Chem. Zentr. 1906, **77**, i, 707) suggests that acetoacetic acid may be detected by the smell of iodoacetone produced on the addition of a solution of iodine ; Lindemann (München med. Woch. **53**, 1019, *see* A. 1906, **90**, ii, 813 ; Chem. Zentr. 1906, **77**, ii, 717) states that the odour evolved on heating urine with iodine is not a characteristic test for acetoacetic acid. Mayer (Pharm. Ztg. **50**, 1001, *see* A. 1906, **90**, ii, 501 ; Chem. Zentr. 1906, **77**, i, 406) pours the urine on to an equal volume of a mixture of 5 c.c. ferric chloride solution in 95 c.c. brine. A claret red ring will be observed if acetoacetic acid is present. If the red colour is only just visible, the liquid may be assumed to contain 0·01% of the acid. By diluting the sample to this extent, therefore, the amount of the acid in the undiluted sample may be determined. The test should be negative if the urine is previously boiled for five minutes. For the estimation of acetone and acetoacetic acid in diabetic urine, *see* Folin (J. Biol. Chem. 1907, **3**, 177); *see also* Goldblatt (Biochem. J. 1925, **19**, 626) and Otto (Pharm. Ztg. 1930, **75**, 479): and for the determination in blood, *see* Cristol (Bull. Soc. chim. biol. 1929, **11**, 731).

Methyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOCH_3$, is prepared by heating methyl acetate with sodium under a reflux condenser and subsequently distilling in a stream of carbon dioxide. It is a colourless liquid, easily miscible with water, b.p. 169°–170° (corr.), d_4^4 1·0917, d_{10}^{10} 1·0855, d_{15}^{15} 1·0809, d_{20}^{20} 1·0766, d_{25}^{25} 1·0724 (Perkin, J.C.S. 1894, **65**, 826). It is decomposed on boiling with water into carbon dioxide, acetone, and methyl alcohol. With ferric chloride it yields a deep red coloration. Methyl acetoacetate semicarbazone has m.p. 152°–153° (Backer and Meyer, Rec. trav. chim. 1926, **45**, 82). Ljunggren (Ber. 1923, **56** [B], 2469) gives the velocity constant 0·01211 for the hydrolysis of methyl acetoacetate with sodium hydroxide.

Ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 \rightleftharpoons CH_3{\cdot}C(OH):CH{\cdot}COOC_2H_5$, was discovered by Geuther in 1863, and independently by Frankland and Duppa in 1865. It is a colourless liquid with a pleasant odour. It has b.p. 180·6°–181·2°/754 mm. (Brühl, Annalen, 1880, **203**, 27); b.p. 180°–180·3°/754·4 mm. (Schiff, Ber. 1886, **19**, 561); b.p. 80°/20 mm. (Dunstan and Stubbs, J.C.S. 1908, **93**, 192); b.p. 181°–182° (corr.) (Perkin, J.C.S. 1892, **61**, 836); $d_{4^\circ}^{20^\circ}$ 1·0256 (Brühl, *l.c.*); $d_{4^\circ}^{0^\circ}$ 1·0465 (Schiff, *l.c.*); $d_{16\cdot3^\circ}^{16\cdot3^\circ}$ 1·0307; $d_{91^\circ}^{91^\circ}$ 0·9839; $d_{70^\circ}^{70^\circ}$ 0·9941; $d_{75^\circ}^{75^\circ}$ 0·9913; $d_{80^\circ}^{80^\circ}$ 0·9888; $d_{85^\circ}^{85^\circ}$ 0·9865; $d_{90^\circ}^{90^\circ}$ 0·9843; $d_{95^\circ}^{95^\circ}$ 0·9824; $d_{100^\circ}^{100^\circ}$ 0·9809 (Perkin, *l.c.* and *ibid.* 1896, **69**, 1172).

The structure of this ester has been the subject of much discussion. It has now been shown to exist in an enolic and a keto form. The composition of freshly prepared ethyl acetoacetate has been found by Meyer (Annalen, 1911, **380**, 212) to be enol 7·71%, keto 92·29%. In solution, the amount of enol present is affected by the solvent and the temperature; a rise in temperature favours the keto form. Knorr, Rothe, and Averbeck (Ber. 1911, **44**, 1139) by cooling a solution of ethyl acetoacetate (in alcohol or other solvents) to −78° found that the keto form could be isolated by crystallisation; it has b.p. 40°–41°/2 mm., n_D^{10} 1·4225, and solidifies at −39°. These workers also obtained the enol form by treating a suspension of the sodium derivative of the ester in petroleum with dry hydrogen chloride, filtering off the sodium chloride, and evaporating the filtrate under low pressure at −78°. The enol form has $d_{4^\circ}^{10^\circ}$ 1·0119, $n_D^{10^\circ}$ 1·4480. When ethyl acetoacetate is distilled, and the distillate cooled to a low temperature, the latter contains 20–30% of the enol form. The enolic form of ethyl acetoacetate has also been prepared by Mingasson (Bull. Soc. chim. 1929 (iv), **45**, 716) by treating the sodium derivative with acetyl chloride in ether. The acetate on hydrolysis with 1% oxalic acid gives the pure enol, d^{17° 1·0379, n^{17° 1·444. The enolic form has been prepared by Meyer and Hopff (Ber. 1921, **54** [B], 579) by distillation of the equilibrium ester containing a trace of phthalic acid using Jena glass apparatus. The distillate, which is collected in a quartz receiver, is refractionated from a silica apparatus. The first fraction is pure enol, $n_D^{10^\circ}$ 1·4475. Meyer and Schoeller (Ber. 1920, **53** [B], 1410), by distilling the mixture from a quartz flask, have obtained the pure keto form as a residue in the flask. Décombe (Ann. Chim. 1932 [X], **18**, 98), by the slow distillation of the equilibrium mixture (7·4% enol) (6–8 drops per minute at 11 mm.), using especially cleaned Pyrex flasks and a fractionating column protected carefully from air currents, obtained 98–99·5% enol, and suggests that the enolisation takes place in the column.

Rumeau (Bull. Soc. chim. 1924 [iv], **35**, 762) finds that the velocity with which the enolic form passes into the equilibrium mixture depends on the presence of other substances, of which some increase and some decrease the velocity. (*See also* Rice and Sullivan, J. Amer. Chem. Soc. 1928, **50**, 3048).

Ethyl acetoacetate is prepared by the action of sodium on ethyl acetate (Wislicenus, Annalen, 1877, **186**, 214): 100 g. of sodium are added to 1000 g. of ethyl acetate, and after the first reaction has moderated, the mixture is heated on a water-bath under a reflux condenser until the sodium has disappeared (2–2½ hours). 550 g. of 50% acetic acid are added to the warm mass, and, after cooling, 500 c.c. water. The upper layer is separated and fractionated: the yield is 175 g. of product, b.p. 175°–185°, and some 350–400 g. of ethyl acetate may be recovered from the lower fractions.

Roberts (J.S.C.I. 1924, **43**, 295T) recommends the use of pure ethyl acetate, clean sodium, and 5% of absolute alcohol for the preparation of ethyl acetoacetate.

Inglis and Roberts (Organic Syntheses, Collective Vol. I, page 230) recommend the use of 50 g. sodium and 500 g. of ethyl acetate, free from water, and containing 2 to 3% of alcohol. The mixture is worked up in the usual way with the addition of 50% acetic acid, and salt is added if necessary to separate the ester layer. Yield 105–110 g., b.p. 76°–80°/18 mm.

Metallic calcium has been used by Perkin and Pratt (J.C.S. 1909, **95**, 161) and sodamide by Titherley (J.C.S. 1902, **81**, 1527) as condensing agents in the preparation of ethyl acetoacetate, but neither of these gives as good yields as sodium.

The work of Snell and McElvain (J. Amer. Chem. Soc. 1931, **53**, 2310) shows that sodium ethoxide gives as good yields as sodium in the preparation of ethyl acetoacetate, and indicates that it is the active condensing agent.

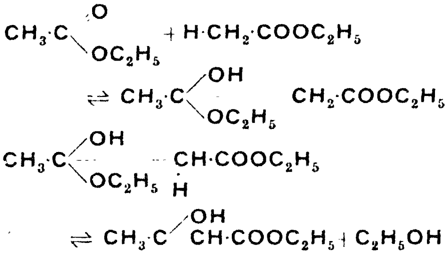
McElvain (J. Amer. Chem. Soc. 1929, **51**, 3124) has found that ethyl acetoacetate may be prepared in good yield from ethyl acetate and sodium ethoxide, by distilling off the alcohol, formed during the reaction, at intervals together with unchanged ester. In this method excess ester was used for this purpose, which was to prevent the reversible reaction from taking place:

$$2RCH_2{\cdot}COOC_2H_5+C_2H_5ONa \rightleftharpoons 2C_2H_5OH \\ +RCH_2{\cdot}C(ONa):CR{\cdot}COOC_2H_5$$

This method was also applied successfully to ethyl propionate and ethyl butyrate. In this way ethyl α-propionylpropionate, b.p. 88°–90° at 12 mm., and ethyl α-butyrylbutyrate, b.p. 102°–105° at 12 mm., were obtained. In the case of higher boiling esters Briese and McElvain (J. Amer. Chem. Soc. 1933, **57**, 1697) found that the reaction could be carried out at such a temperature that under the reduced pressure used the ethyl alcohol was removed by distillation as soon as it was formed. The following keto esters ($RCH_2{\cdot}CO{\cdot}CHR{\cdot}COOEt$) were prepared by this method :

Ester used.	β-keto ester.	B.p. (5 mm.).	d^{25}_{25}	n^{25}_{D}
Ethyl valerate	ethyl α-valerylvalerate	109°-110°	0·9330	1·4306
Ethyl caproate	ethyl α-caproylcaproate	132°-133°	0·9203	1·4351
Ethyl heptoate	ethyl α-heptoylheptoate	147°-148°	0·9107	1·4386
Ethyl caprylate	ethyl α-caprylylcaprylate	173°-175°	0·9047	1·4418
Ethyl pelargonate	ethyl α-pelargonyl-pelargonate	195°-200°		
Ethyl caprate	ethyl α-caprylcaprate	220°-225°		
Ethyl laurate	ethyl α-lauryllaurate	m.p. 28°-29°		
Ethyl myristate	ethyl α-myristylmyristate	m.p. 37°-38°		

With regard to the mechanism of the acetoacetic ester condensation, the work of Cox, Kroeker, and McElvain (J. Amer. Chem. Soc. 1934, **56**, 1173) indicates that it is best interpreted by an extension of the aldol condensation (*cf.* Michael, J. pr. Chem. 1888 [ii], **37**, 483) :



$$CH_3{\cdot}C\begin{matrix}\nearrow O\\ \searrow OC_2H_5\end{matrix} + H{\cdot}CH_2{\cdot}COOC_2H_5 \rightleftharpoons CH_3{\cdot}C\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}\quad CH_2{\cdot}COOC_2H_5$$

$$CH_3{\cdot}C\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}\text{---}\ \text{--}\begin{matrix}CH{\cdot}COOC_2H_5\\ \dot{H}\end{matrix} \rightleftharpoons CH_3{\cdot}C\begin{matrix}\diagup OH\\ \ \end{matrix}\ CH{\cdot}COOC_2H_5 + C_2H_5OH$$

Ethyl acetoacetate is neutral to litmus ; it gives a violet coloration with ferric chloride and a crystalline addition product with sodium bisulphite. It forms metallic derivatives with sodium and other metals. Thus when treated with sodium dissolved in absolute alcohol it gives the sodio derivative of the enolic form, which yields the alkyl derivative of the keto form on treatment with an alkyl halogen compound :

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + C_2H_5ONa$$
$$\rightarrow CH_3{\cdot}C(ONa):CH{\cdot}COOC_2H_5 + C_2H_5OH$$
$$CH_3{\cdot}C(ONa):CH{\cdot}COOC_2H_5 + RI$$
$$\rightarrow NaI + CH_3{\cdot}CO{\cdot}CHR{\cdot}COOC_2H_5$$

A second alkyl group may be introduced by treating the mono-alkyl derivative with sodium (in alcohol) and alkyl halide (the two groups cannot be introduced in one stage) :

$$CH_3{\cdot}C(ONa):CR{\cdot}COOC_2H_5 + R_1I$$
$$\rightarrow NaI + CH_3{\cdot}CO{\cdot}CRR_1{\cdot}COOC_2H_5$$

These compounds hydrolyse in two ways, giving either acids or ketones :

(*a*) hydrolysis with strong alkali gives the alkyl acetic acid :

$$CH_3{\cdot}CO{\cdot}CHR{\cdot}COOC_2H_5$$
$$\rightarrow CH_3{\cdot}COOH + RCH_2{\cdot}COOH + C_2H_5OH$$

(*b*) Hydrolysis with dilute acid or dilute alkali gives the ketone :

$$CH_3{\cdot}CO{\cdot}CRR_1{\cdot}COOC_2H_5$$
$$\rightarrow CH_3{\cdot}CO{\cdot}CRR_1H + C_2H_5OH + CO_2$$

The bromination of ethyl acetoacetate has been found by Pedersen (J. Physical Chem. 1933, **37**, 751) to take place in four stages. In the first stage the ethyl acetoacetate is enolised ; in the second the enolic form is brominated to the keto form of ethyl α-bromacetoacetate :

$$CH_3{\cdot}C(OH):CH{\cdot}COOC_2H_5$$
$$\xrightarrow{Br_2} CH_3{\cdot}CO{\cdot}CHBr{\cdot}COOC_2H_5$$

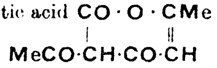
In the third stage the bromo derivative is enolised ; in the fourth this is brominated to ethyl αα-dibromoacetoacetate :

$$CH_3{\cdot}C(OH):CBr{\cdot}COOC_2H_5$$
$$\xrightarrow{Br_2} CH_3{\cdot}CO{\cdot}CBr_2{\cdot}COOC_2H_5$$

Only the first and third stages take place with measurable velocity.

Yanagisawa and Kamio (J. Pharm. Soc. Japan, 1921, 240) give a method for the estimation of ethyl acetoacetate with sodium sulphite.

Ethyl acetoacetate loses alcohol on refluxing and forms dehydracetic acid



$$\begin{matrix} & & CO\cdot O\cdot CMe\\ & & |\qquad\quad \| \\ MeCO{\cdot} & & CH{\cdot}CO{\cdot}CH\end{matrix}$$

(Arndt and Nachtwey, Ber. 1924, **57**, 1489).

Reduction with sodium amalgam gives β-hydroxy butyric acid,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$$

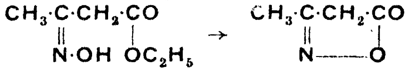
(Wislicenus, Annalen, 1869, **149**, 207).

Ethyl acetoacetate semicarbazone,

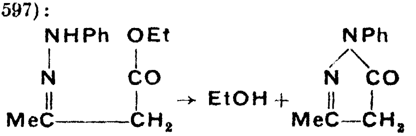
$$CH_3{\cdot}C(:N{\cdot}NH{\cdot}CONH_2)CH_2{\cdot}COOC_2H_5,$$

has m.p. 129° (Thiele and Stange, Annalen, 1894, **283**, 29).

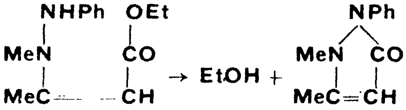
Ethyl acetoacetate is used in the synthesis of ring compounds :—(1) with hydroxylamine (Hantzsch, Ber. 1891, **24**, 495) it gives methyl *iso*-oxazolone, owing to internal condensation :



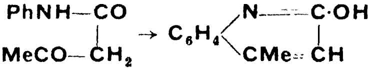
(2) With phenyl hydrazine it gives 1-phenyl-3-methyl-5-pyrazolone (Knorr, Ber. 1883, **16**, 2597) :



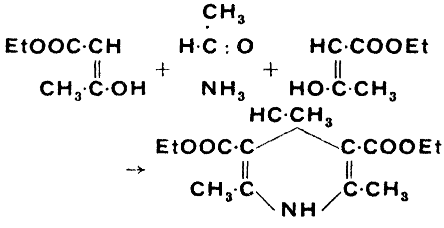
Antipyrin (1-phenyl-2 : 3-dimethyl-5-pyrazolone) may be prepared by the methylation of the above phenylmethylpyrazolone, or by condensing ethyl acetoacetate with methylphenylhydrazine (Knorr, Ber. 1884, **17**, 549, 2037; Annalen, 1887, **238**, 203):



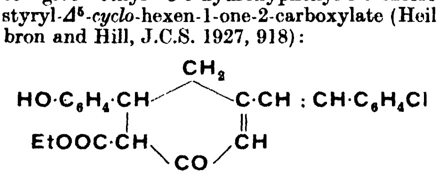
(3) Ethyl acetoacetate when heated with aniline gives the anilide; this on treatment with concentrated sulphuric acid gives 2-hydroxy-4-methylquinoline (Knorr, Annalen, 1886, **236**, 83):



(4) Pyridines may be obtained by condensing ethyl acetoacetate with aldehyde ammonias (Hantzsch, Annalen, 1882, **215**, 7); thus ethyl dihydrocollidine dicarboxylate may be obtained from acetaldehyde ammonia:



(5) Ethyl acetoacetate condenses with 2-hydroxystyryl methyl ketone to give 4-acetonyl-2-methyl-γ-pyran, m.p. 134°–135° (Forster and Heilbron, J.C.S. 1924, **125**, 340). (6) It condenses with 2′-chloro-2-hydroxydistyryl ketone to give ethyl 3-*o*-hydroxyphenyl-5-*o*-chlorostyryl-Δ⁶-*cyclo*-hexen-1-one-2-carboxylate (Heilbron and Hill, J.C.S. 1927, 918):



(7) Glyoxal and ethyl acetoacetate give ethyl formyl-methylenebisacetoacetate,

$$CHO{\cdot}CH[CH(CO{\cdot}CH_3){\cdot}COOC_2H_5]_2,$$

m.p. 109°–110°, together with an oil containing furan derivatives (West, J. Amer. Chem. Soc. 1925, **47**, 2780).

ALKYL DERIVATIVES OF ETHYL ACETOACETATE.

I. Mono-substituted Alkyl Derivatives.—*Ethyl methylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CHMeCOOEt$$

b.p. 186·8°, d^{6° 1·009 (Geuther, Jahresber. über Chemie, 1863, **16**, 324; 1865, **18**, 303). *Ethyl ethylacetoacetate*, $CH_3{\cdot}CO{\cdot}CHEtCOOEt$, b.p. 197·7°–198·8° (corr.), $d^{4^\circ}_{4^\circ}$ 0·9937, $d^{15^\circ}_{15^\circ}$ 0·9838 (Perkin, J.C.S. 1892, **61**, 837); d^{12° 0·998 (Geuther, *l.c.*). *See also* Frankland and Duppa (Annalen, 1866, **138**, 215) and Wislicenus (Annalen, 1877, **186**, 187). *Ethyl propylacetoacetate*, $CH_3{\cdot}CO{\cdot}CHPr^{\alpha}{\cdot}COOEt$, b.p. 208°–209°, $d^{0^\circ}_{4^\circ}$ 0·981 (Burton, Amer. Chem. J. 1881–82, **3**, 385), b.p. 208° (Perkin and Pratt, J.C.S. 1909, **95**, 162). *Ethyl* iso*propylacetoacetate*, $CH_3{\cdot}CO{\cdot}CHPr^{\beta}COOEt$, b.p. 201° at 758·4 mm., d^{0° 0·9805 (Frankland and Duppa, Annalen, 1868, **145**, 78; Bischoff, Ber. 1895, **28**, 2620). *Ethyl* iso*butylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CHBu^{\beta}{\cdot}COOEt,$$

b.p. 217°–218°, $d^{17\cdot5}$ 0·951 (Rohn, Annalen, 1878, **190**, 306).

Ethyl amylacetoacetate,

$$CH_3{\cdot}CO{\cdot}CH(C_5H_{11})COOEt,$$

b.p. 242°–244° (Ponzio and Prandi, Gazzetta, 1898 (2), **28**, 280). *Ethyl* iso*amylacetoacetate*, $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CHMe_2)COOEt$, b.p. 227°–228° (Peters, Ber. 1887, **20**, 3322), b.p. 234°–235°/767 mm. (Bischoff, Ber. 1895, **28**, 2627). *Ethyl heptylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CH(C_7H_{15})COOEt,$$

b.p. 271°–273°, $d^{17\cdot7}$ 0·9324 (Jourdan, Annalen, 1880, **200**, 105).

Ethyl octylacetoacetate,

$$CH_3{\cdot}CO{\cdot}CH(C_8H_{17})COOEt,$$

b.p. 280°–282°, $d^{18\cdot5^\circ}_{17\cdot5^\circ}$ 0·9354 (Guthzeit, Annalen, 1880, **204**, 2).

II. Disubstituted Alkyl Derivatives.—*Ethyl dimethylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CMe_2{\cdot}COOEt,$$

b.p. 184°, d^{16° 0·9913 (Frankland and Duppa, Annalen, 1866, **138**, 328); b.p. 184·8°–185°, $d^{4^\circ}_{4^\circ}$ 0·9915, $d^{10^\circ}_{10^\circ}$ 0·9857, $d^{15^\circ}_{15^\circ}$ 0·9813, $d^{20^\circ}_{20^\circ}$ 0·9773, $d^{25^\circ}_{25^\circ}$ 0·9736 (Perkin, J.C.S. 1894, **65**, 827). *Ethyl methylethylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CMeEt{\cdot}COOEt,$$

b.p. 198°, $d^{22^\circ}_{17\cdot5^\circ}$ 0·974 (Saur, Annalen, 1877, **188**, 260); b.p. 200°–201° (Wislicenus, Annalen, 1883, **219**, 308). *Ethyl methylpropylacetoacetate*, $CH_3{\cdot}CO{\cdot}CMePr{\cdot}COOC_2H_5$, b.p. 214°, d^{15° 0·9585 (Liebermann and Kleemann, Ber. 1884, **17**, 918); b.p. 215°–217°, $d^{17^\circ}_{4^\circ}$ 0·9575 (Jones, Annalen, 1884, **226**, 287). *Ethyl diethylacetoacetate*, $CH_3{\cdot}CO{\cdot}CEt_2{\cdot}COOEt$, b.p. 218° (Wislicenus, Annalen, 1877, **186**, 191); b.p. 215°–216° (corr.), $d^{4^\circ}_{4^\circ}$ 0·9832, $d^{10^\circ}_{10^\circ}$ 0·9782, $d^{15^\circ}_{15^\circ}$ 0·9743, $d^{20^\circ}_{20^\circ}$ 0·9708, $d^{25^\circ}_{25^\circ}$ 0·9674 (Perkin, J.C.S. 1894, **65**, 827). *Ethyl dipropylacetoacetate*, $CH_3{\cdot}CO{\cdot}CPr^{\alpha}{}_2{\cdot}COOEt$, b.p. 235°–236°, $d^{0^\circ}_{4^\circ}$ 0·9584 (Burton, Amer. Chem. J. 1881–82, **3**, 386). *Ethyl diïsobutylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}CBu^{\beta}{}_2{\cdot}COOEt,$$

b.p. 250°–253°, d^{10° 0·947 (Mixter, Ber. 1874, **7**, 501). *Ethyl diheptylacetoacetate*,

$$CH_3{\cdot}CO{\cdot}C(C_7H_{15})_2{\cdot}COOEt,$$

b.p. 331°–333°, $d^{17\cdot5°}$ 0·8907 (Jourdan, Annalen, 1880, **200**, 114). *Ethyl dioctylacetoacetate*,

$$CH_3\cdot CO\cdot C(C_8H_{17})_2\cdot COOEt,$$

b.p. 340°–342° ; b.p. 263°–265° at 90 mm. (Guthzeit, Annalen, 1880, **204**, 9).

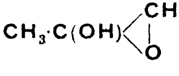
J. N. E. D.

ACETOCAUSTIN. Trade name for trichloroacetic acid, $CCl_3\cdot COOH$. Caustic.

ACETOL (hydroxyacetone, acetylcarbinol, propan-*α*-ol-*β*-one), $CH_3\cdot CO\cdot CH_2\cdot OH$, is obtained in the pyrochemical decomposition of glycerol (Nef, Annalen, 1904, **335**, 247), and is prepared (1) by hydrolysis of the ester obtained by condensing chloro- or bromo-acetone with potassium acetate or formate (Perkin, J.C.S. 1891, **59**, 786 ; Nef, *l.c.* ; Levene and Walki, Organic Syntheses, 1930, **10**, 1) ; and (2) by heating for 10–15 hours *α*-bromopropaldehyde with a methyl alcoholic solution of an alkali formate (Nef, *l.c.*).

Acetol is a colourless liquid with a pleasant odour ; a taste sweet at first, becoming burning ; it polymerises on keeping but is stable if mixed with an equal volume of methyl alcohol ; it is miscible with water, alcohol, or ether. It has the following physical constants : f.p. −17°, b.p. 145°–146°/760 mm. with slight decomposition (Kling, Ann. Chim. 1905 [viii], **5**, 496), 105°–106°/200 mm. (Perkin, *l.c.*), 96°–97°/150 mm., 54°/18 mm. (Nef, *l.c.*) ; d_{20}^{20} 1·0824, n_D^{20} 1·4295 (Kling, *l.c.*).

Acetol reduces Fehling's solution and ammoniacal solutions of silver in the cold. Oxidation with Fehling's solution, with copper sulphate and alkali, or with copper acetate yields chiefly lactic acid (Nef, *l.c.* ; Denis, Amer. Chem. J. 1907, **38**, 583) ; whilst silver oxide oxidises it quantitatively into equimolecular quantities of acetic and formic acids (Denis, *l.c.*). When acetol is reduced by sodium amalgam in alkaline solution it yields propylene glycol and isopropyl alcohol ; when the reduction is effected in acid or neutral solution propylene glycol and acetone are produced ; these reactions suggest that acetol exists in aqueous solution in the tautomeric form,



$$CH_3\cdot C(OH)\begin{matrix}\diagup CH_2\\ \quad |\\ \diagdown O\;\end{matrix}$$

(Kling, Compt. rend. 1902, **135**, 970). Acetol is phytochemically reduced by yeast in the presnece of sugar to *l*-propyleneglycol, b.p. 186°–188°, $[\alpha]_D$ −20·48° in aqueous solution (Farber, Nord, and Neuberg, Biochem. Z. 1920, **112**, 313). The following characteristic derivatives of acetol are described : the crystalline compound with sodium bisulphite, $C_3H_6O_2,NaHSO_3$ (Kling, Ann. Chim. 1905 [viii], **5**, 500) ; the *oxime*, m.p. 71° (Piloty and Ruff, Ber. 1897, **30**, 2059) ; the *semicarbazone*, m.p. 195°–200° ; the *phenylhydrazone*, m.p. 106° ; the *oxazone*, m.p. 153°–154° (Nef, *l.c.*) ; the p-*nitrophenylhydrazone*, m.p. 190°–191° ; the p-*bromophenylhydrazone*, m.p. 128–130° (Palazzo and Caldarella, Atti R. Accad. Lincei, 1905 [v], **14**, ii, 151) ; the *methyl ether*, colourless liquid, b.p. 118°, d^{20} 0·9570 ; the *ethyl ether*, b.p. 128°, d^{21} 0·9204 (Henry, Compt. rend. 1881, **93**, 421) ; the p-*nitrophenylhydrazone* of the *methyl ether* melts at 110°–111°, that of the *ethyl ether* at 101°–102° (Leonardi and de Franchis, Gazzetta, 1903, **33**, i, 316) ; the *acetate*, a sweet-smelling oil, b.p. 73°–74°/18 mm., yields the *oxime*, b.p. 118°–119°/16 mm., the *semicarbazone*, m.p. 145°, the p-*nitrophenylhydrazone*, m.p. 144°, and the p-*bromophenylhydrazone*, m.p. 137°–138° (Palazzo and Caldarella, *l.c.*).

A delicate specific test for acetol is its conversion into 3-*hydroxy*-2-*methylquinoline* by boiling for a few minutes in dilute aqueous solution containing sodium hydroxide and *o*-aminobenzaldehyde ; the mixture is cooled, acidified, and made alkaline again with sodium bicarbonate and yields a fluorescent solution giving the quinoline derivative on extraction with ether. It is obtained as a colourless solid, which gives a deep red colour with ferric chloride in alcoholic solution, and a brilliant blue fluorescence on dilution with water (Baudisch, Biochem. Z. 1918, **89**, 279). This reaction can also be used as a delicate test for carbohydrates, which yield acetol on distilling nearly to dryness an aqueous solution (0·1 g. in 100 c.c.) with solid sodium hydrogen carbonate (5 g.) (Baudisch and Deuel, J. Amer. Chem. Soc. 1922, **44**, 1585).

The name "Acetol" has also been applied to the salicylate of acetylcarbinol,

$$CH_3\cdot CO\cdot CH_2O\cdot CO\cdot C_6H_4\cdot OH,$$

m.p. 71° (Fritsch, B.P. 3961 (1893), J.S.C.I. 1894, 274).

M. A. W.

ACETOMORPHINE HYDROCHLORIDE, *diamorphine hydrochloride*, *heroin hydrochloride* are synonyms for diacetylmorphine hydrochloride, a very soluble powder, m.p. 229°–233°. Used as a sedative.

ACETONAPHTHONE, methyl-naphthyl ketone, $CH_3\cdot CO\cdot C_{10}H_7$, m.p. 51·5°, b.p. 295°–296°, known as "orange crystals," has a definite odour of orange blossoms and is useful in sweet pea and convolvulus perfumes. It is preferred by many perfumers to methyl anthranilate, as it does not impart a fluorescence to the perfumes in which it is used.

E. J. P.

ACETONE. Dimethyl ketone, $CH_3\cdot CO\cdot CH_3$, is produced by destructive distillation of acetates (Dumas, Ann. Chim. Phys. 1831 [ii], **49**, 208 ; Zeise, Annalen, 1840, **33**, 32 ; Hägglund and Hedman, J. pr. Chem. 1924 [ii], **107**, 50), and is found in the pyroligneous acid produced by distillation of wood (Völckel, Annalen, 1851, **80**, 310 ; J.S.C.I. 1897, **16**, 667, 722 ; 1908, **27**, 798). It is also formed by distillation of carbohydrates with lime (Fremy, Annalen, 1835, **15**, 279), by pyrolysis of citric acid, and by various other pyrolytic reactions, and has been prepared synthetically from zinc methyl and acetyl chloride (Freund, Annalen, 1860, **118**, 11). Acetone has been produced on a commercial scale by distillation of the giant kelp of the Pacific coast, but is now chiefly manufactured either by Weizmann's fermentation process or from acetylene (*see also* ACETYLENE and FERMENTATION). Yamada (J. Soc. Chem. Ind. Japan, 1933, **36**, 193) has examined a method of preparation by oxidation of moist acetaldehyde.

Preparation.—Acetone is conveniently prepared in the laboratory by dry distillation of barium or calcium acetate, the latter requiring a higher temperature and yielding a less pure product. Becker (J.S.C.I. 1907, **26**, 279) has outlined conditions for an improved yield. Magnesium and strontium acetates can also be used. Industrially, the method is modified by passing the vapour of acetic acid into air-tight vessels heated to 500° containing lime or baryta mounted on a suitable carrier (J.S.C.I. 1899, **18**, 824 ; G.P. 81914), or by passing a continuous current of pyroligneous acid over a heated acetate (*Patents*, J.S.C.I. 1906, **25**, 634 ; 1907, **26**, 1002 ; 1908, **27**, 277 ; Wenghoffer, G.P. 144328 ; J.S.C.I. 1903, **22**, 297) or by passing alcohol over manganese dioxide heated to 540° (Donath, Chem.-Ztg. 1927, **51**, 924). Acetone may be separated from wood spirit by distillation over calcium chloride. The distillate is treated with sodium bisulphite solution, the addition product separated, recrystallised, and then distilled with sodium carbonate. Acetone is separated from the distillate by treatment with concentrated calcium chloride solution, extraction with ether, drying, and fractionation of the extract.

Acetone is found in the blood and urine of persons in abnormal pathological conditions. The general pharmacology of acetone has been investigated by Salart and Kleitmann (Bull. Soc. Exptl. Med. 1921, **18**, 202).

Purification.—Various workers have suggested alternative methods for purification. Conroy (J.S.C.I. 1900, **19**, 206) and Dott (*ibid.* 1908, **27**, 272) recommend distillation from sulphuric acid, whilst Arnoult (*ibid.* p. 679) advocates treatment with oxidising agents (*see also* U.S.P. 1542538). Shipsey and Werner (J.C.S. 1913, **103**, 1255) prepare a crystalline addition compound, $NaI \cdot C_3H_6O$, by boiling the acetone with anhydrous sodium iodide and this readily liberates acetone on gentle warming. Duclaux and Lanzenberg (Bull. Soc. chim. 1920, **27**, 779) suggest the formation of a constant boiling mixture with carbon disulphide, b.p. 39°, as convenient if methyl alcohol is absent. Werner (Analyst, 1933, **58**, 335) removes impurities of aldehydes and unsaturated compounds by shaking 700 c.c. acetone for 10 minutes in a stoppered bottle with 3 g. silver nitrate in 20 c.c. water and 20 c.c. *N*-sodium hydroxide solution, separating, drying, and fractionating the purified acetone.

Properties.—Acetone is a colourless, mobile liquid with a pleasant and characteristic odour. It is highly inflammable and forms explosive mixtures with air and oxygen (Payman, J.S.C.I. 1918, **37**, 406R ; Berl and Fischer, Z. Elektrochem. 1924, **30**, 29 ; Jones and Klick, Ind. Eng. Chem. 1929, **21**, 791). It burns with a white, smokeless flame. It has b.p. 56·3° (Regnault) ; d^{0} 0·8144, $d^{13\cdot9}$ 0·79045 (Kopp, Annalen, 1847, **64**, 214) ; b.p. 56·1°–56·2° (Shipsey and Werner, *l.c.*) ; 56·22° (corr.) and d_4^{0} 0·81858 (Thorpe, J.C.S. 1880, **37**,. 212) ; m.p. –94·9° (Ladenberg and Krügel, Ber. 1899, **32**, 1821). More recent physical data are recorded by Prud'homme (J. Chim. phys. 1920, **18**, 307) ; Felsing and Durban (J. Amer. Chem. Soc. 1926, **48**, 2885) and Zmaczyński (Rocz. Chem. 1933, **13**, 192). Eckart (Brennstoff-Chem. 1923, **4**, 24) gives $n_D^{20°}$ 1·35998. Electrical conductivity data are due to Creighton and Way (J. Franklin Inst. 1918, **186**, 675).

Acetone is miscible in all proportions with water, alcohol, ether, and many other organic liquids, and may be salted out of aqueous solution by addition of calcium chloride. Physical data for acetone-water mixtures are given by Rakshit (Reprint Indian Assoc. Cultiv. Sci. 1917, **3**, 1) and Nicholls (Analyst, 1929, **54**, 2, 9).

When acetone vapour is passed through a red-hot copper tube, a very small proportion of tarry substance is obtained, containing naphthalene, and a large volume of gas, consisting mainly of carbon monoxide, methane, hydrogen, and ethylene (Barbier and Roux, Compt. rend. 1886, **102**, 1559); pyrolysis in a platinum tube at 1,100° gives ketene, together with methane, carbon monoxide, and ethylene (Peytral, Bull. Soc. chim. 1922 [iv], **31**, 122), while Berl and Kullmann (Ber. 1932, **65** [B], 1114) have shown that the yield of ketene varies between 25 and 75% according to the temperature and catalyst. The optimum temperature is about 700° and the most successful catalysts are oxides of vanadium, thorium or chromium, or aluminium carbide on pumice. A yield of 90% is claimed by Al (Z. angew. Chem. 1932, **45**, 545) using vanadium pentoxide on pumice as catalyst. Freudenheim (J. Physical Chem. 1918, **22**, 184) has postulated a series of consecutive reactions to account for the products of pyrolysis. Acetone, when heated under pressure at 300°, yields a mixture of hydrocarbons containing a large proportion of di-*iso*butylene (Petrov and Ivanov, J. Russ. Phys. Chem. Soc. 1930, **12**, 1489). It is reduced by hydrogen in the presence of platinum to propane, and with iron-platinum to *iso*propyl alcohol (Faillebin, Ann. Chim. 1925, **4**, 156, 410).

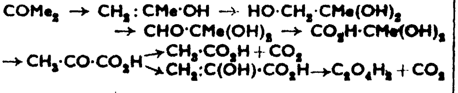
Acetone forms condensation products in the presence of various dehydrating agents ; thus, when heated for a considerable time with baryta, diacetone alcohol is formed (Organic Syntheses, 1, 45 ; U.S.P. 1654103), which on treatment with lime, or distillation in the presence of iodine, yields mesityl oxide and phorone (Fittig, Annalen, 1859, **110**, 32 ; Organic Syntheses, **1**, 53). Similar products are formed in a catalytic process described by Maihle and de Godon (Bull. Soc. chim 1917 [iv], **21**, 61) and are also formed by prolonged standing with hydrogen chloride (Baeyer, Annalen, 1866, **140**, 297) or by distillation with concentrated sulphuric acid ; in the latter case, however, mesitylene, *iso*durene, and other substances are also formed (Orndorff and Young, Amer. Chem. J. 1896, **15**, 249) ; treatment with boron trifluoride yields similar results, while with zinc chloride, products of a terpenoid character are formed (Raikow, Ber. 1897, **30**, 905). The reactions with nitric acid, nitric oxide (Newbury and Orndorff, Amer. Chem. J. 1894, **12**, 517), hydrogen peroxide (Baeyer and Villiger, Ber. 1899, **32**, 3625 ; 1900, **33**, 174, 858), thionyl chloride (Loth and Michaels, Ber. 1894, **27**, 2540), and hypophosphorous acid

(Marie, Compt. rend. 1901, **133**, 219) have also been studied.

Acetone is reduced by sodium in the presence of water to *iso*propyl alcohol and pinacone (Fittig, Annalen, 1859, **110**, 25 ; 1860, **114**, 54 ; Städeler, Annalen, 1859, **111**, 277 ; Friedel, *ibid.* 1862, **124**, 329), but when air is excluded and the materials are quite dry, sodium acetone, $CH_2:CMe{\cdot}ONa$, is formed (Freer, Amer. Chem. J. 1894, **12**, 355 ; 1895, **13**, 308 ; 1896, **15**, 582 ; Taylor, J.C.S. 1906, **89**, 1258 ; Bacon and Freer, Philippine J. Sci. 1907, **2**, 67). The sodium derivative is also formed when acetone is treated with sodamide in liquid ammonia (Strain, J. Amer. Chem. Soc. 1930, **52**, 2827).

Red-hot magnesium acts on acetone, yielding hydrogen and allylene, whilst magnesium amalgam forms magnesium acetone which is rapidly decomposed by water, yielding pinacone hydrate (Keiser, Amer. Chem. J. 1897, **18**, 328 ; Couturier and Meunier, Compt. rend. 1905, **140**, 721). Anhydrous acetone, in presence of metallic calcium, is slowly converted at the ordinary temperature into mesityl oxide (Raikow, Chem.-Ztg. 1913, **37**, 1455). Chlorine, bromine, and iodine in the presence of alkalis convert acetone into chloroform, bromoform, and iodoform respectively.

Reactions.—When quite pure acetone should remain perfectly colourless on exposure to light, and should not be attacked by potassium permanganate in the cold ; in the presence of alkali, however, and on warming, carbonic and oxalic acids are formed (Cochenhausen, J. pr. Chem. 1900, [ii], **166**, 451 ; Conroy, J.S.C.I. 1900, **19**, 206 ; Fournier, Bull. Soc. chim. 1908 [iv], **3**, 259). According to Witzemann (J. Amer. Chem. Soc. 1917, **39**, 2657), the oxidation process involves preliminary enolisation of the acetone, followed by the formation of pyruvic acid :



$$COMe_2 \rightarrow CH_2:CMe{\cdot}OH \rightarrow HO{\cdot}CH_2{\cdot}CMe(OH)_2 \rightarrow CHO{\cdot}CMe(OH)_2 \rightarrow CO_2H{\cdot}CMe(OH)_2 \rightarrow CH_3{\cdot}CO{\cdot}CO_2H \begin{cases} \rightarrow CH_3{\cdot}CO_2H + CO_2 \\ \rightarrow CH_2:C(OH){\cdot}CO_2H \rightarrow C_2O_4H_2 + CO_2 \end{cases}$$

Detection.—Treatment with ozone yields formaldehyde and formic acid (Briner and Meier, Helv. Chim. Acta, 1929, **12**, 529). Acetone readily yields iodoform with aqueous potash and iodine (Lieben). Gunning (Z. anal. Chem. 1886, **24**, 147) has modified this reaction to render it sensitive when alcohol is present by employing ammonia and a solution of iodine in ammonium iodide (*see also* Kolthoff, Pharm. Weekblad, 1925, **62**, 652). Another test proposed by Reynolds (Z. anal. Chem. 1886, **24**, 147) is based on the fact that mercuric oxide is soluble in acetone in the presence of potassium hydroxide ; the suspected liquid is mixed with a solution of mercuric chloride rendered strongly alkaline with alcoholic potash, and after shaking the mixture is filtered and the filtrate tested for mercury by means of ammonium sulphide or stannous chloride. Denigès (Compt. rend. 1898, **126**, 1868 ; 1899, **127**, 963 ; Bull. Soc. chim. 1895 [iii], **13**, 543 ; 1898 [iii], **19**, 754) recommends the use of the additive compound formed by acetone with mercury sulphate, for detecting acetone in methyl and ethyl alcohol (Oppenheimer, Ber. 1899, **32**, 986). Penzoldt (Z. anal. Chem. 1886, **24**, 147) adds to the suspected liquid *o*-nitrobenzaldehyde, which in presence of caustic alkali combines with acetone to form indigo (*see also* Raw, J.S.C.I. 1932, **51**, 276T). Another delicate test is to add sodium hydroxide, hydroxylamine, and pyridine, then ether and bromine until the solution is yellow; hydrogen peroxide is now added, when, if acetone is present, the solution becomes blue (Stock) ; dimethyl *p*-phenylenediamine produces a red coloration which changes to violet on addition of alkali or acid (Malerba, Z. anal. Chem. 1898, **37**, 690). Similar colour reactions are obtained by adding a few drops of sodium nitroprusside to a mixture of acetone and a primary aliphatic amine (Rimini, Chem. Zentr. 1898, II, 132 ; Lefmann and Pines, A. 1929, 1425). Of all these tests, Lieben's is perhaps the most sensitive. To detect acetone in urine a strong solution of sodium nitroprusside is added and the mixture made alkaline with potash, when a red coloration is produced which changes to violet on addition of acetic acid (Legal, J. Pharm. Chim. 1888, **17**, 206 ; Denigès, Bull. Soc. chim. 1896 [3], **15**, 1058); according to Bäck (Wien. klin. Wochenschr. 1917, **30**, 465) sulphuric acid may replace the acetic acid in this test. Egeling (Chem. Zentr. 1894, II, 457) states that aldehyde also responds to this test, and that Nobel's modification of the test, in which the caustic alkali is replaced by ammonia, is more trustworthy (*see also* van Urk, Pharm. Weekblad, 1925, **62**, 2, 8). Kolthoff (*ibid.* 1918, **55**, 1021) describes a modified Fabinyi-Frommer test which is claimed to be both sensitive and specific. Other methods are described using 2 : 4-dinitrophenylhydrazine (Bülow, Science, 1925, **61**, 344) ; furfuraldehyde and sulphuric acid (Tschelincev and Nitikin, Bull. Soc. chim. 1933, **53**, 1130) ; ethylenediamine hydrate (Faught, " Essentials of Laboratory Diagnosis " ; Schaeffer, Amer. J. Pharm. 1926, **98**, 643). The iodoform and vanillin tests have been re-examined by Korenmann (Z. anal. Chem. 1933, **93**, 335, 438) and Le Fèvre and Pearson (J.S.C.I. 1932, **51**, 433T), who assert that Raw's test is not specific, as ethyl pyruvate, and acetophenone and its derivatives also give the colour. A modified Scott-Wilson test is described by Kline (Arh. Hemiju, 1931, **5**, 212 ; Bull. Soc. chim. biol. 1932, **14**, 885). Pittarelli (Policlinico, 1921, **28**, 621) has drawn attention to the fact that a substance liberated by steam from rubber connections gives many of the characteristic reactions of acetone.

Summaries of important tests are given by Lillig (Pharm. Ztg. 1919, **64**, 696) ; Ind. Eng. Chem. 1926, **18**, 863 ; and Leffman (Amer. J. Pharm. 1929, **101**, 337). For further methods of detecting and estimating acetone, compare Arachequesne, Compt. rend. 1890, **110**, 642 ; Collischonn, Z. anal. Chem. 1890, **29**, 562 ; Squibb, J. Amer. Chem. Soc. 1896, **18**, 1068 ; Kebler, *ibid.* 1897, **19**, 316 ; Schwicker, Chem.-Ztg. 1891, **15**, 914 ; Strache, Monatsh. 1892, **13**, 299 ; Klar., J.S.C.I. 1896, **15**, 299 ; Hintz, Z.

anal. Chem. 1888, **27**, 182 ; Sternberg, Chem. Zentr. 1901, I, 270 ; Keppeler, Z. angew. Chem. 1905, **18**, 464 ; Vaubel and Schleuer, *ibid.* p. 214 ; Jolles, Ber. 1906, **39**, 1306 ; Auld, J.S.C.I. 1906, **25**, 100 ; Heikel, Chem.-Ztg. 1908, **32**, 75.

Estimation.—There are two principal methods for estimating acetone ; the first consists in converting the acetone to iodoform using a measured volume of a standard solution of iodine in aqueous potassium iodide and titrating the excess. Various modifications are described (Hubbard, J.C.S. 1917, **111**, 494 ; Ljungdahl, Biochem. Z. 1917, **83**, 103 ; Hermans, Chem. Weekblad, 1921, **18**, 348 ; Söderlund, Svensk Kem. Tidskr. 1922, **34**, 152 ; Lesničenko, Chem. Obzor. 1932, **7**, 2). In the second a solution of acetone is treated with a freshly prepared solution of pure hydroxylamine hydrochloride and the hydrochloric acid liberated is estimated by titration with standard alkali (Bennett and Donovan, Analyst, 1922, **47**, 146 ; Marasco, Ind. Eng. Chem. 1926, **18**, 701 ; Krajčinović, Chem.-Ztg. 1931, **55**, 894). Other methods are based on the use of mercuric sulphate (Ionescu *et al.*, Bull. Soc. chim. Romania, 1923, **5**, 15 ; Meyer and Mathey, Compt. rend. 1930, **191**, 490) ; Nessler reagent (Bougault and Gros, J. Pharm. Chim. 1922, **26**, 170 ; Gros, Ann. Falsif. 1925, **18**, 39). Determination in the presence of other materials, such as methyl alcohol, acetaldehyde, acetoacetic ester, etc., is described by Field, Ind. Eng. Chem. 1918, **10**, 552 ; Hoepner, Z. Nahr. Genussm. 1917, **34**, 453 ; Goodwin, J. Amer. Chem. Soc. 1920, **42**, 39 ; Stepp, and Engelhardt, Biochem. Z. 1920, **111**, 8 ; Stepp and Friedrich, Z. physiol. Chem. 1921, **116**, 293 ; Ljunggren, Skand. Arch. Physiol. 1925, **46**, 325. Microchemical methods of determination are described by Kober, J.S.C.I. 1918, **37**, 75T (nephelometric) ; Richter-Quittner, Biochem. Z. 1919, **93**, 163 ; Ljungdahl, *ibid.* 1919, **96**, 325 (iodometric) ; Thomas, Bull. Soc. Stiinte Cluj, 1925, **2**, 299 ; Lindeberg, Compt. rend. Soc. Biol. 1933, **114**, 15.

For estimating acetone in wood spirit, *see* Arachequesne, *l.c.* ; Vignon, Compt. rend. 1890, **110**, 534 ; 1891, **112**, 873 ; and in urine, *see* Huppert, Z. anal. Chem. 1890, **29**, 632 ; Salkowski, J. Pharm. Chim. 1891, 194 ; Geelmuyden, Z. anal. Chem. 1896, **35**, 503 ; Willen, Chem. Zentr. 1897, II, 134 ; Martz, II, 232 ; Argenson, Bull. Soc. chim. 1896 [3], **15**, 1055 ; Studer, Chem. Zentr. 1898, II, 1152 ; Mallat, J. Pharm. 1897, 6296 ; Sabbatani, Chem. Zentr. 1899, II, 22 ; Riegler, Z. anal. Chem. 1901, **40**, 94 ; Vournasos, Bull. Soc. chim. 1904 [iii], **31**, 137 ; Graaff, Pharm. Weekblad, 1907, 44, 555 ; Folin, J. Biol. Chem. 1907, **3**, 177 ; Monimart, J. Pharm. Chem. 1892, **26**, 392 ; Heikel, *l.c.* ; Hart, J. Biol. Chem. 1908, **4**, 477.

Derivatives.—Acetone combines directly with a large number of substances yielding well-characterised additive compounds. 1. *Compounds with metallic salts* :—Acetone forms compounds with mercuric sulphate (Denigès, *l.c.* ; Oppenheimer, *l.c.*), with mercuric oxide (Auld and Hantzsch, Ber. 1905, **38**, 2677 ; Lasserre, J. Pharm. Chim. 1890, **22**, 246), with mercuric cyanide (Marsh and Struthers, J.C.S. 1905, **87**, 1878), with mercuric iodide (Gernez, Compt. rend. 1903, **137**, 255 ; Marsh and Struthers, Proc. Chem. Soc. 1908, 266), and with mercuric nitrate (Hofmann, Ber. 1898, **31**, 2212). Acetone forms definite crystalline compounds when shaken with concentrated solutions of the acid sulphites (bisulphites) of the alkali metals (Precht, Phot. Centr. 1902, **8**, 301 ; Kerp, Kaiserl. Gesundh. 1904, **21**, 40 ; Rothwood, Monatsh. 1905, **26**, 1545). The *potassium* salt, $Me_2CO,KHSO_3$, and the *sodium* salt, $Me_2CO,NaHSO_3$, crystallise in nacreous scales (Limpricht, Annalen, 1855, **93**, 238) ; the *ammonium* salt, Me_2CO,NH_4HSO_3, crystallises in laminæ (Städeler, Annalen, 1859, **111**, 307). The *barium* salt has the formula $2Me_2CO,Ba(SO_3H)_2,H_2O$ (Fagard, J. Pharm. Chim. 1895, **2**, 145). These salts yield acetone when heated with aqueous potash. *Calcium chloride* combines with acetone to form $CaCl_2,2Me_2CO$ and $CaCl_2,Me_2CO$ (Bagster, J.C.S. 1917, **111**, 494); with Reinecke salt (Dudley, Biochem. J. 1933, **27**, 157) ; and with zinc bromide and iodide (Coucoulesco, Bull. Soc. chim. Romania, 1924, **6**, 36). The solubilities of various metallic salts in acetone are described by Zapata y Zapata (Anal. Fís. Quím. 1930, **28**, 605) and Lannung (Z. physikal Chem. 1932, **161**, 255, 269). 2. *Compounds with chloroform* (Willgerodt, Ber. 1881, **14**, 2451 ; **15**, 2308 ; Cameron and Holly, Chem. Zentr. 1898, II, 277 ; Jocitsch, *ibid.* 1899, I, 606 ; Willgerodt and Dürr, J. pr. Chem. 1889 [ii], **39**, 283), and with *carbon disulphide* (Wertheim, J. Amer. Chem. Soc. 1931, **53**, 4037). 3. *Compounds with hydrogen cyanide* (Urech, Annalen, 1872, **164**, 255) :—Acetone yields acetone-cyanohydrin, C_4H_7NO, b p. 120°, when added to anhydrous hydrogen cyanide ; and diacetone cyanohydrin, $C_7H_{13}NO_2$, a crystalline substance, when treated with a 25% solution (aqueous) of hydrogen cyanide (Tiemann and Friedländer, Ber. 1881, **14**, 1965) ; with 3·3% hydrogen cyanide acetone-cyanhydrin is obtained in the dark, but in the light a mixture of products is formed (Silber, Ber. 1905, **38**, 1671). Acetone cyanohydrin may also be obtained by treating a mixture of acetone and aqueous potassium cyanide with sulphuric acid at a temperature not exceeding 20° (Welch and Clemo, J.C.S. 1928, 2629 ; *see also* Organic Syntheses, **11**, 4). Its reaction with phosphorus chlorides is described by Chrzaszczewska and Sobieranski (Rocz. Chem. 1927, **7**, 470). 4. *Compounds with ammonia* :—Ammonia unites with acetone in the cold with the elimination of the elements of water ; the reaction, however, proceeds more quickly if the temperature is raised to 100°, or if dry ammonia gas is passed into boiling acetone. Several bases, diacetonamine $C_6H_{13}NO$, triacetonamine $C_9H_{17}NO$, triacetondiamine $C_9H_{20}N_2O$, and dehydrotriacetonamine $C_9H_{15}N$, the last two in very small quantity only, have been obtained by these methods, the relative proportions in which they are formed varying with the temperature and time employed. These bases and their derivatives have been examined by Heintz (Annalen, 1874, **174**, 133 ; **175**, 252 ; 1875,

178, 305, 326 ; 1876, **181**, 70 ; **183**, 276 ; 1877, **189**, 214 ; **191**, 122 ; 1879, **198**, 42, 98 ; 1880, **201**, 90 ; **203**, **336**) and by Sokoloff and Latschinoff (Ber. 1874, **7**, 1384), Ruhemann and Carnegie (J.C.S. 1888, **53**, 424), Rügheimer (Ber. 1888, **21**, 3325 ; 1892, **25**, 1562), Harries (Annalen, 1897, **296**, 328), Franchimont and Friedmann (Rec. trav. chim. 1907, **26**, 223), Gabriel and Colman (Ber. 1902, **35**, 3805), Kohn and Lindauer (Monatsh. 1902, **23**, 754), Kohn (Annalen, 1907, **351**, 134 ; Monatsh. 1903, **24**, 765, 773 ; 1904, **25**, 135, 817, 850 ; 1907, **28**, 429, 508, 529, 537, 1040), Patterson and Macmillan (J.C.S. 1921, **119**, 269) ; they yield crystalline salts, and can be separated from one another by means of their oxalates. Methylamine also gives corresponding compounds with acetone, but dimethylamine yields dimethyldiacetonamine as the sole product (Göttschmann, Annalen, 1879, **197**, 27). Hock and Stuhlmann (Ber. 1928, **61**B, 470) claim to have obtained a crystalline molecular addition product of acetone and ammonia, m.p. −41°.

Acetoxime, m.p. 59°–60°, b.p. 135°, has been prepared in the usual way (Meyer and Janny, Ber. 1882, **15**, 1324 ; Landrieu, Compt. rend. 1905, **140**, 1392) and as a by-product in the preparation of hydroxylamine (Semon, J. Amer. Chem. Soc. 1923, **45**, 188 ; Organic Syntheses, **3**, 61). *Acetone semicarbazone* melts at 187° and the *benzylsemicarbazone* at 155° (Leboucq, J. Pharm. Chim. 1930 [viii], **11**, 200). *Acetone phenylhydrazone* is a liquid, b.p. 115°–120° (Staudinger and Gaule, Ber. 1916, **49**, 1905) ; 124°–125° (Curtius and Pflug, J. pr. Chem. 1891 [ii], **44**, 543) ; *see also* Sutherland and Wilson, J.C.S. 1924, **125**, 2145 ; Ardagh and Williams, J. Amer. Chem. Soc. 1925, **47**, 2976 ; when treated with bromine it yields the *p*-bromo derivative, m.p. 155° (Humphreys, J.C.S. 1923, **123**, 1766). The 2 : *5-dibromophenylhydrazone*, m.p. 85°–86°, is described by Votoček and Lukes (Bull. Soc. chim. 1924 [iv], **35**, 868) ; and other substituted hydrazones by Votoček and Rys (Coll. Czech. Chem. Comm. 1929, **1**, 346).

Thioacetones have been studied by Baumann and Fromm (Ber. 1889, **22**, 1035, 2592). Metallic derivatives of the type $CH_3{\cdot}CO{\cdot}CH_2K$ are obtained by the electrolysis of acetone solutions of potassium or sodium iodides or of potassium thiocyanate (Levi and Voghera, Gazzetta, 1905, **35**, i, 277).

Acetone yields substitution derivatives when acted upon with chlorine or bromine (Bischoff, Ber. 1872, **5**, 863, 963 ; 1875, **8**, 1329). The following derivatives have been obtained :— *Monofluoroacetone* is produced by treating chloroacetone in ether with thallium fluoride and then heating under reflux ; it boils at 72° (Ray and others, Nature, 1933, **132**, 749). *Trifluoroacetone*, prepared by Swarts (Bull. Acad. roy. Belg. 1927 [v], **13**, 175) by boiling ethyl trifluoroacetoacetate with sulphuric acid (*idem*, *ibid.* 1926 [v], **12**, 692), has b.p. 21·9° and yields a monohydrate, m.p. 51° ; semicarbazone, m.p. 127° ; and oxime, m.p. −1·5°, b.p. 102°–103°. *Monochloroacetone* (Henry, Ber. 1872, **5**, 190 ; Mulder, *ibid.*, p. 1009 ; Barbaglia, Ber. 1874, **7**, 467 ; Linnemann, Annalen, 1865, **134**, 171 ; Koenigs and Wagstaffe, Ber. 1893, **26**, 554 ; Wislicenus, Kircheisen, and Sattler, *ibid.* 1893, **26**, 908 ; Fritsch, *ibid.*, p. 597 ; Tcherniac, Ber. 1892, **25**, 2629 ; Kling, Bull. Soc. chim. 1905 [3], **33**, 322) ; 2 : 4-*dinitrophenylhydrazone*, m.p. 124°–125°. Unsymmetrical *dichloroacetone* (Fittig, Annalen, 1859, **110**, 40 ; Borsche and Fittig, Annalen, 1865, **133**, 112 ; Erlenbach, Annalen, 1892, **269**, 46 ; Tcherniac, *l.c.* ; Fritsch, *l.c.* ; McIntosh, J.C.S. 1905, 790 ; U.S.P. 1916979). Symmetrical *dichloroacetone* (Barbaglia, *l.c.* ; Fritsch, *l.c.*) ; *semicarbazone*, m.p. 120°. *Trichloroacetone* (Bischoff, *l.c.* ; Kraemer, Ber. 1874, **7**, 252 ; Perrier and Prost, Compt. rend. 1905, **140**, 146 ; Hantzsch, Ber. 1898, **21**, 242). *Tetrachloroacetone* (Bischoff, Levy, Witte, and Curchod, Annalen, 1889, **252**, 330 ; **254**, 83 ; Levy and Jedlicka, Ber. 1888, **21**, 318). *Pentachloroacetone* (Cloëz, Bull. Soc. chim. 1883 [2], **39**, 638 ; Fritsch, Annalen, 1894, **279**, 310 and *l.c.* ; Levy and Jedlicka, *l.c.*). Pentachloroacetone treated with phosphorus pentachloride yields *as*-heptachloropropane, C_3HCl_7, a crystalline substance, m.p. 32° ; also obtained by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride (Böeseken and Prins, Proc. K. Akad. Wetensch. Amsterdam, 1911, **13**, 685). Homberger and Borries (Science, 1920, **52**, 206) find three distinct steps in the chlorination and three fractions in the product : *see also* U.S.P. 1436940. s-*Dichloroacetone* has been prepared by oxidation of $\alpha\gamma$-dichloro-*iso*propyl-alcohol with acid dichromate (Conant and Quayle, Organic Syntheses, **2**, 13), while treatment of acetone with a mixture of nitric and hydrochloric acids below 50° gave chlor-*iso*nitrosoacetone (Boyd, J.S.C.I. 1925, **44**, 222T). The corresponding bromo-derivatives, with the exception of tribromoacetone, are obtained by the direct action of bromine upon acetone (Mulder, Jahresb. 1864, 330 ; McIntosh, *l.c.* ; Lapworth, J.C.S. 1904, **85**, 33), also by other methods (Hjelt and Siven, Ber. 1888, **21**, 3288 ; Norton and Wistenhoff, Amer. Chem. J. 1893, **10**, 213 ; Hantzsch, *l.c.*). *Monobromoacetone*, b.p. 23·5°–24·5°/3·5 mm., is prepared by the action of bromine and sodium bromate in aqueous solution on acetone in the presence of sulphuric acid (Chrzaszczewska and Sobieranski, Rocz. Chem. 1927, **7**, 79 ; *see also* Organic Syntheses, **10**, 12) ; it yields a cyanohydrin, b.p. 94·5°–95·5°/5·5 mm., and finds application in chemical warfare (Heritage, Mech. Eng. 1919, **41**, 806 ; Dufraisse and Bongrand, Compt. rend. 1920, **171**, 817). Other halogen derivatives (J.S.C.I. 1897, **16**, 933 ; Hantzsch, *l.c.* and Ber. 1889, **22**, 1238) and the compounds of acetone with the halogen acids (Archibald and McIntosh, J.C.S. 1904, **85**, 924) have been described.

Acetone forms a large number of condensation products and derivatives with other organic compounds : *Cyanoacetones* (Hantzsch, Ber. 1890, **23**, 1472 ; Tcherniac, Ber. 1892, **25**, 2607, 2621 ; Komppa, Ber. 1900, **33**, 3530). *Acetone dioxalic ester* obtained by the action of sodium ethoxide on a mixture of acetone and oxalic ester is converted when treated with sodium ethoxide to a dienolic substance forming lemon-yellow needles, m.p. 98°, and dyeing wool in alcoholic solution. It is the first nitrogen-free dyestuff of the fatty series to be obtained (Willstätter and Pummerer, Ber. 1904, **37**, 3733). *Pseudo*cyclo*citralidene acetone* and its homologues have an odour of violets, and are suitable for use in perfumes (J.S.C.I. 1905, **24**, 290).

For *acetone dicarboxylic acid* and its derivatives, *see* Ormerod, Proc. Chem. Soc. 1906, 205 ; Denigès, Compt. rend. 1899, **128**, 680 ; Lippmann, Ber. 1908, **41**, 3981 ; ester, Organic Syntheses, **5**, 53 ; for *acetonyl acetone* and its derivatives, *see* Knorr, Ber. 1889, **22**, 168, 2100 ; Claisen and Ehrhardt, Ber. 1889, **22**, 1009 ; Zincke and Kegel, Ber. 1890, **23**, 230 ; Claisen, Ber. 1892, **25**, 3164 ; the azo- (Bülow and Schlotterbeck, Ber. 1902, **35**, 2187) and diazo-derivatives of acetonyl acetone have dyeing properties (Favrel, Compt. rend. 1899, **128**, 318).

Acetone, with benzene diazonium chloride in the presence of alkali, yields a compound $C_{15}H_{14}ON_2$, m.p. 134°–135°, which has dyeing properties (Bamberger and Wulz, Ber. 1901, **24**, 2793). For other condensation products compare Boessneck, Ber. 1888, **21**, 1906 ; Pechmann and Wehsarg, *ibid.* 2989, 2994 ; Franke and Kohn, Monatsh. 1898, **19**, 354 ; **20**, 876 ; Spier, Ber. 1898, **28**, 2531 ; Perkin and Thorpe, J.C.S. 1896, **73**, 1482 ; Weidel, Monatsh. 1896, **17**, 401 ; Micko, *ibid.* 442 ; Stobbe, Ber. 1895, **28**, 1122 ; Cornelson and Kostanecki, Ber. 1896, **29**, 240 ; Claisen, *ibid.* 2931 ; Röhmer, Ber. 1898, **31**, 281 ; Pfitzinger, J. pr. Chem. 1897, **56**, 283 ; Freer, Amer. Chem. J. 1897, **17**, 1 ; Barbier and Bouveault, Compt. rend. 1893, **118**, 198 ; Haller and March, Compt. rend. 1904, **139**, 99 ; Straus, Ber. 1904, **37**, 3293 ; Harries and Ferrari, Ber. 1903, **36**, 656 ; Ulpiani and Bernardini, Atti R. Accad. Lincei, 1904, **13**, 331 ; Pechmann and Sidgwick, Ber. 1904, **37**, 3816 ; Duntwitz, Monatsh. 1906, **27**, 773 ; Knoevenagel, Ber. 1906, **39**, 3451, 3457 ; Purdie, J.C.S. 1906, **89**, 1200 ; Richard, Compt. rend. 1907, **145**, 129. Diacetones and their derivatives have been studied by Combes (Compt. rend. 1889, **108**, 1252 ; Béhal and Auger, Compt. rend. 1889, **109**, 970 ; Claisen and Stylos, Ber. 1888, **21**, 141) ; derivatives of triacetone by Weinschenk (Ber. 1901, **34**, 2185). Acetone forms addition products with cresols (Berl and Schwebel, Z. angew. Chem. 1922, **35**, 189 ; Weissenberger and Piatti, Monatsh. 1924, **45**, 187 ; Schuster and Henke, *ibid.* 1925, **46**, 325).

Applications.—Acetone finds extensive use in the artificial silk industry as a solvent for cellulose acetate. It dissolves many fats and resins and also acetylene and tannins (Trimble and Peacock, Pharm. J. **58**, 317 ; Butler, J.S.C.I. 1921, **40**, 25T). It is used in pharmacy and perfumery, in the manufacture of smokeless powders (J.C.S.I. 1896, **15**, 231), of cordite and celluloid articles (Marshal, J.S.C.I. 1904, **23**, 24, 645), and also in the preparation of iodoform (Teeple, J. Amer. Chem. Soc. 1904, **26**, 170 ; Abbott, J. Phys. Chem. **7**, 83) ; of chloroform (Squibb, J. Amer. Chem. Soc. 1896, **18**, 231 ; Orndorff and Jessel, Amer. Chem. J. 1893, **10**, 363 ; Dolt, *l.c.*, p. 271 ; Feyer, Z. Elektrochem. 1919, **25**, 115). It has been used as a substitute for alkali in photographic developers containing sulphite (Lumière and Segewetz, Bull. Soc. chim. 1896 [3], **15**, 1164 ; Eichengrün, Z. angew. Chem. 1902, **15**, 1114). Schmitt (Petroleum Times, 1922, **8**, 249) suggests the use of equal parts of acetone and sulphur dioxide for extracting the soluble substances from coal and lignite. The uses are summed up by Remler in his book "Acetone, its Properties and Uses" (Bradford, Pa., 1924), and in an article in the New York Chemical Age, 1923, **31**, 342.

ACETONE-CHLOROFORM, *aaa*-trichlor-*tert*butyl alcohol (Chloretone),

$$(CH_3)_2 \cdot C(OH) \cdot CCl_3,$$

is prepared by the action of potassium hydroxide on a cooled mixture of acetone and chloroform (Willgerodt, J. pr. Chem. 1888 [ii], **37**, 361). It is a white crystalline compound of camphor-like odour ; m.p. 97° (anhyd.), b.p. 167°. It is readily volatile in steam and small quantities can be thus readily detected (Aldrich, J. Biol. Chem. 1918, **34**, 263). It is sparingly soluble in cold water, soluble in hot, and decomposed by water at 180° (Willgerodt, Ber. 1882, **15**, 2305). It crystallises well from ether, alcohol, acetic acid, acetone, or chloroform. Acetone-chloroform is reduced by zinc dust and alcohol to dichloro*iso*butylene, *iso*crotylchloride, and *iso*butylene (Jocitsch, J. Russ. Phys. Chem. Soc. 1898, **30**, 920). The chlorine in acetone-chloroform can be replaced wholly or partially by phenyl residues on treatment with benzene in the presence of aluminium chloride ; analogous compounds are obtained with toluene or *p*-xylene (Willgerodt, J. pr. Chem. 1888 [ii], **37**, 361). Acetone-chloroform is used as a germicide, a surgical dressing, a hypnotic (Aldrich and Houghton, Amer. J. Physiol. 1900, **3**, 26), a specific for sea-sickness (Merck, Ann. Report, 1907, 1), and a local anæsthetic (Cohn, Pharm. Zentr. H. 40, 33). It is also known as "nautisan" and is the chief ingredient of "zotos" and "anesin."

Wolffenstein, Loewy, and Bachstez (Ber. 1915, **48**, 2035) have prepared a number of esters of acetone-chloroform and examined their pharmacology; they find that most of them are unchanged in the organism, and that they frequently have a totally different action from that of the alcohol, usually causing convulsions.

ACETONEDICARBOXYLIC ACID, *β*-keto-glutaric acid, $CO(CH_2 \cdot COOH)_2$, is obtained from citric acid by warming it with fuming sulphuric acid. The sparingly soluble double salt of basic mercuric sulphate with mercuric acetone-dicarboxylate,

$$SO_4 \cdot [HgO]_2 \cdot Hg \cdot 2CO \cdot [CH_2 \cdot COO]_2Hg,$$

forms a delicate test for a citrate (Denigès' test), which is carried out by oxidising citric acid with permanganate in the presence of an acid solution of mercuric sulphate (*v.* KETONES).

ACETONE OIL is the residual liquid remaining after the separation of acetone from the products of the dry distillation of calcium acetate. It can also be prepared by the dry distillation of the lime salts obtained by neutralising fleece washings (suint) with milk of lime (*see* Buisine, J.S.C.I. 1899, **18**, 292 ; 1902, **21**, 164 ; P. Baechlin, Rev. Chim. Ind. **9**, 112 ; **15**, 240). It is a slightly-coloured liquid, d^{15} 0·830–0·835, having a penetrating smell and acrid, burning taste. Acetone oil from suint contains at least 90% of ketones, 75% of which are soluble in water and consist mainly of methyl ethyl ketone ; the oil obtained from calcium pyrolignate consists largely of methyl propyl, and methyl *iso*propyl ketones (A. and P. Buisine, Compt. rend. 1898, **126**, 351 ; 1899, **128**, 561). It has been used as a denaturant of alcohol.

From yellow acetone oil, b.p. 60°–250°, Suida and Pöll (Z. angew. Chem. 1927, **40**, 505 ; Monatsh. 1927, **48**, 167) isolated the following ketones, acetone, methyl ethyl ketone, methyl *iso*propyl ketone, methyl propyl ketone, methyl butyl ketone, methyl *iso*butyl ketone, mesityl oxide, propyl *iso*propyl ketone, methyl *a*-methylpropyl ketone, methyl *a*-ethylpropyl ketone, 3-methyl-Δ^3-hexen-5-one, and methyl *n*-amyl ketone (*see also* Pringsheim *et al.*, B. 1927, 720).

ACETOPHENONE, phenyl methyl ketone, *hypnone*, $C_6H_5{\cdot}CO{\cdot}CH_3$, occurs in coal tar and can be isolated therefrom in the form of its *p*-bromophenylhydrazone derivative (Weissgerber, Ber. 1903, **36**, 754 ; Herzenberg and Winterfeld, Ber. 1931, **64** [B], 1025). It is prepared by the action of acetyl chloride on benzene in the presence of aluminium chloride or ferric chloride (Bouveault, Bull. Soc. chim. 1897 [iii], **17**, 1020 ; Boeseken, Rec. trav. chim. 1901, **20**, 105 ; Nencki and Stoeber, Ber. 1897, **30**, 1768) or by distilling an equimolecular mixture of calcium acetate and benzoate. Its catalytic production from acetic and benzoic acids with the aid of manganous oxide or thorium dioxide is described by Lakomkin (J. Appl. Chem. Russia, 1930, **3**, 555 ; 1931, **4**, 176 ; A. 1931, 354 ; 1932, 478). Acetophenone crystallises in large plates, m.p. 19·66° (Livingstone, Morgan, and Lammert, J. Amer. Chem. Soc. 1924, **46**, 881 ; Foote and Leopold, Amer. J. Sci. 1926 [v], **11**, 42), b.p. 202° and d_4^{25} 1·02382. Its density at various temperatures has been detormined by Perkin (J.C.S. 1896, **69**, 1200) and Eijkman (Chem. Zentr. 1904, I. 1259), the vapour pressure by Kahlbaum (Z. physikal. Chem. 1898, **26**, 612), and the refractive index for various wave lengths by Feussner (Z. Physik, 1927, **45**, 689). The dipole moment is $2{\cdot}97 \times 10^{-18}$ (Hassel and Naeshagen, Z. physikal. Chem. 1929, B, **4**, 217). Acetophenone has an odour resembling bitter almonds, is insoluble in water but dissolves readily in alcohol, ether, chloroform, and benzene.

It forms an *oxime*, m.p. 60°, a *phenylhydrazone*, m.p. 105°, p-*nitrophenylhydrazone*, m.p. 184°–185°, p-*bromophenylhydrazone*, m.p. 111°–112°, a *semicarbazone*, m.p. 201°, a *thiosemicarbazone*, m.p. 108°, and a *hydrazone*, m.p. 255° ; the *diethyl acetal* has b.p. 114°/23 mm., d_0^0 0·9266. It forms *acetophenone ammonia*, $\mathrm{CMePh(N:CMePh)_2}$, m.p. 115° (Thomae, Arch. Pharm. 1906, **244**, 643) (*v.* KETONES), and a large number of condensation products with aldehydes, halogens, acids, mercury salts, etc.

Acetophenone is readily oxidised by potassium permanganate to phenylglyoxalic acid (Glücksmann, Monatsh. 1890, **11**, 246). The main product of reduction by sodium and alcohol or by electrolysis is methylphenyl carbinol ; with hydrogen and nickel, ethylbenzene can also be obtained (Darzens, Compt. rend. 1904, **139**, 868). Several tests for its micro-detection are proposed by Behrens (Chem.-Ztg. 1902, **26**, 1152). Acetophenone is used as a soporific (Dujardin-Beaumetz and Bardet, Compt. rend. 1885, **101**, 960 ; Pharm. J. 1886, 582) and as a solvent for cellulose ethers (Noll, Papier-Fabr. 1929, **25**, 497 ; U.S.P. 1467098).

Aminoacetophenones are used as dye intermediates (Morgan and Moss, J.S.C.I. 1923, **42**, 461T). According to Camps (Arch. Pharm. 1902, **240**, 15) o-*aminoacetophenone*, b.p. 250°–252°, has anæsthetic properties which are destroyed by condensing it with benzaldehyde, tolualdehyde, or cinnamaldehyde, but not with aldehydes containing phenolic hydroxyl (Hildebrandt, Chem. Zentr. 1905, II. 502 ; Scholtz and Huber, Ber. 1904, **37**, 390). m-*Aminoacetophenone*, m.p. 99·5°, *oxime*, m.p. 192°–194°, p-*Aminoacetophenone*, m.p. 106°, b.p. 293°–295°.

m-*Nitroacetophenone* is obtained by direct nitration. It is a light yellow solid, softening at 74° and melting at 76°–78° (Corson and Hagen, Organic Syntheses, **10**, 74 ; **11**, 102 ; Baker and Moffitt, J.C.S. 1931, 314).

2 : 4 : 6 : *Trinitroacetophenone*, m.p. 90°–92°, is obtained from 2 : 4 : 6 : trinitrobenzaldehyde and diazomethane (Sonn and Bülow, Ber. 1925, **58**B, 1691).

p-*Bromoacetophenone* is obtained from bromobenzene by the action of aluminium chloride and acetic anhydride or acetyl chloride (Adams and Noller, Organic Syntheses, **5**, 17).

Benzalacetophenone is formed from acetophenone and benzaldehyde (Kohler and Chadwell, Organic Syntheses, **2**, 1).

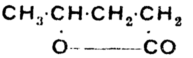
β-ACETOPROPIONIC ACID. Lævulic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. This acid is obtained by the action of dilute acids on a number of carbohydrates, *see* Grote and Tollens (Ber. 1874, **7**, 1376), Fischer and Hirschberger (*ibid.* 1889, **22**, 370), Smith and Tollens (*ibid.* 1900, **33**, 1286), Grote, Kehrer, and Tollens (Annalen, 1881, **206**, 207), Grote and Tollens (*ibid.* 1881, **206**, 226), Rodewald and Tollens (*ibid.* 1881, **206**, 231), Kent and Tollens (*ibid.* 1885, **227**, 228), Rischbiet and Tollens (*ibid.* 1886, **232**, 193), and Wehmer and Tollens (*ibid.* 1888, **243**, 314).

It is also formed by the oxidation of the terpene alcohols, and by the hydrolysis of various nucleic acids (Kossel and Neumann, Ber. 1894, **27**, 2215; Inouye, Z physiol. Chem. 1904, **42**, 117 ; Levene, *ibid.* 1904, **43**, 199).

Lævulic acid is prepared in 42% yield from sucrose (250 g.) by heating in an autoclave with 6·5% hydrochloric acid (600 c.c.) for one hour at 162° under a pressure of 7 atm. The residual cake of humus material is then evaporated to dryness and extracted with ether. After removal of the ether, the residue is distilled under reduced pressure, and the fraction b.p.

120°–130°/4·5 mm. redistilled. It has b.p. 106°–108°/2 mm., n^{40} 1·4342 (Thomas and Schuette, J. Amer. Chem. Soc. 1931, **53**, 2328). Sah and Ma (*ibid.* 1930, **52**, 4881) prepare lævulic acid from glucose (500 g.) by boiling for twenty-four hours under reflux with 1,000 c.c. of diluted (1 : 1) hydrochloric acid, the humus material which separates being filtered off from time to time. After removal of the hydrochloric acid by distillation, the residue is distilled under reduced pressure. The fraction b.p. 146°–184°/7 mm. is collected and redistilled. The distillate on cooling gives crystals of lævulic acid, m.p. 33°–35° ; b.p. 245°–246 °; b.p. 145°/4 mm. 1000 g. glucose give 150 g. acid. *See also* Organic Syntheses, 1929, **9**, 50.

Lævulic acid is very soluble in water, alcohol, and ether. It is not attacked by bromine in the cold ; iodine and sodium hydroxide form iodoform under these conditions. Nitric acid converts it into carbon dioxide, acetic, succinic and oxalic acids. Hydriodic acid and phosphorus at 200° convert it into normal valeric acid ; sodium amalgam forms γ-valerolactone,



$$\begin{array}{l}CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2\\ \quad\;\; O\text{———}CO\end{array}$$

which yields normal valeric acid in acid solution (Wolff, Annalen, 1881, **208**, 104). Iodic acid converts it into diiodoacetoacrylic acid (Angeli and Chiussi, Ber. 1892, **25**, 2205). It decomposes over sulphuric acid in a vacuum, giving a residue which is stated to be dihydroxyvaleric acid (Berthelot and André, Compt. rend. 1896, **123**, 341). It forms a *semicarbazone*, m.p. 187°, and a *dinitrophenylhydrazone*, m.p. 92°.

For the condensation of lævulic acid with aldehydes, *see* Sen and Roy (J. Indian Chem. Soc. 1930, **7**, 401) ; and with benzil, *see* Japp and Murray (Chem. Soc. Proc. 1896, **146**). For the reaction of mono- and dibromolævulic acid with thiocarbamide, *see* Conrad and Schmidt (Annalen, 1895, **285**, 203) ; for dibromolævulic acid, *see* Wolff (Ber. 1893, **26**, 2216) ; for the formation of *cyclo*-pentane derivatives of this bromo-acid, *see* Wolff and Rüdel (Annalen, 1897, **294**, 188).

Lævulic acid is employed on a manufacturing scale as a mordant instead of acetic acid, as it possesses the advantage of being non-volatile with steam.

Grünhut (Z. Nahr. Genussm. 1921, **41**, 261) gives details for the detection and estimation of lævulic acid in foods, also in the presence of formic, acetic and lactic acids.

Gault and Salomon (Compt. rend. 1922, **174**, 754) give the following method of preparation of α-alkyl-lævulic acids : the sodio derivative of diethyl malonate and bromoacetone give diethyl acetonylmalonate, b.p. 150°/20 mm. When the sodio derivative of the latter is treated with an alkyl iodide the alkylacetonylmalonic ester is obtained; this on hydrolysis gives the corresponding acid, which on heating loses carbon dioxide and gives the alkyl-lævulic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CHR{\cdot}COOH$.

Esters.—The *methyl*, *ethyl*, and *propyl* esters of lævulic acid have been prepared by Grote, Kehrer, and Tollens (Annalen, 1881, **206**, 207). For the hydrolysis of ethyl lævulate, *see* Skrabal, Pfaff, and Airoldi (Monatsh. 1924, **45**, 141). Sah and Ma (J. Amer. Chem. Soc. 1930, **52**, 4882) give the following properties of esters of lævulic acid (prepared by treating the acid with excess of the corresponding alcohol in the presence of hydrochloric acid) :

Ester.	B.p.	d_4^{20}	n_D^{20}	Semicarbazone m.p.	Phenylhydrazone m.p.
Methyl . .	191°–193°	1·05113	1·4231	142°–143°	94°–96°
Ethyl . .	199°–201°	1·01336	1·4225	147°–148°	103°–104°
iso-Propyl . .	203°–205°	0·98422	1·4220	141°–142°	108°–109°
n-Propyl . .	214°–216°	0·98988	1·4255	129°–130°	88°–90°
iso-Butyl . .	222°–224°	0·97047	1·4264	112°–113°	84°–86°
n-Butyl . .	229°–231°	0·97452	1·4290	102°–103°	79°–81°
iso-Amyl . .	238°–240°	0·95921	1·4310	91°–92°	70°–72°

Schuette and Cowley (J. Amer. Chem. Soc. 1931, **53**, 3485) also give figures for the refractive indices and densities of a series of esters which do not in every case coincide with those given above. These investigators add figures for the calculated boiling-points at 760 mm.

	n_D^{20}	d_4^{20}	B.p. (calc.).
Methyl .	1·4223	1·05145	197·7°
Ethyl .	1·4218	1·01346	206·2°
n-Propyl .	1·4251	0·99007	221·2°
iso-Propyl.	1·4211	0·98005	208·2°
n-Butyl .	1·4283	0·97350	237·8°
iso-Butyl .	1·4251	0·96926	229·9°
n-Amyl .	1·4316	0·96357	253·2°
iso-Amyl .	1·4294	0·95827	247·9°
n-Hexyl .	1·4343	0·95332	266·8°

Cowley and Schuette (*ibid.* 1933, **55**, 387) prepared the *n*-heptyl, *n*-octyl, *n*-nonyl, and *n*-decyl esters of lævulic acid by treating the acid (1·1 mols.) with the alcohol (1 mol.) containing 3% hydrogen chloride. Carbon tetrachloride was added as a solvent, and to remove the water as it was formed by distillation. The ester fraction contained some acid, which was removed with dry powdered sodium carbonate, followed by fractionation under reduced pressure.

Ester.	n^{20}	d_4^{20}	Molecular refraction.	B.p. at 760 mm (calc.).
n-Heptyl	1·4360	0·94332	59·365	283·5°
n-Octyl	1·4380	0·93635	63·754	291·1°
n-Nonyl	1·4400	0·93360	68·386	298·0°
n-Decyl	1·4417	0·92653	73·141	306·5°

These esters tend to decompose at their boiling-points under ordinary pressure.

Benzyl lævulate has been prepared by Sah, Lei, and Fang (*ibid.* 1933, **55**, 4727) by boiling lævulic acid (52 g.), benzyl alcohol (160 g.), and toluene (4 [illegible] g.) containing dry hydrogen chloride (7 [illegible] r 24 hours under reflux. The toluer [illegible] then distilled off and the residue [illegible] ated under reduced pressure. Yield [illegible] benzyl lævulate, b.p. 181°–183°/17 mm., $d_{4°}^{20°}$ 1·0935; $d_{4°}^{25°}$ 1·0895; $n_D^{20°}$ 1·5090; $n_D^{25°}$ 1·5070. It was characterised by the following: *phenylhydrazone*, m.p. 91°–92°, p-*tolylhydrazone*, m.p. 99°–100°, p-*chlorophenylhydrazone*, m.p. 106°–107°, and p-*bromophenylhydrazone*, m.p. 103°.

Allyl lævulate, b.p. 133°–136°/40 mm., $d_{4°}^{20°}$ 1·0277, $n_D^{20°}$ 1·4413, has been prepared (Sah and Ma, *ibid.* 1932, **54**, 3271) by the direct esterification of the acid using dry hydrogen chloride. The *semicarbazone* has m.p. 126°–127°, and the *phenylhydrazone* m.p. 79°–80°.

Salts.—The *calcium*, *silver*, *sodium*, *copper*, *barium*, *magnesium* and *nickel* salts of lævulic acid have been described by Grote, Kehrer, and Tollens (Annalen, 1881, **206**, 207). Proskouriakoff (J. Amer. Chem. Soc. 1933, **55**, 2132) gives details for the preparation of the calcium, magnesium, *cadmium*, nickel and *manganese* salts from the solution obtained by the acid treatment of sugars (Sah and Ma, *l.c.*) without the isolation of the acid. The mixture is filtered, the hydrochloric acid distilled off, and five volumes of water added, the black tar which separates is removed by filtration, the filtrate treated with charcoal and refiltered, and the clear solution used for the preparation of the salts.

The solubility of calcium lævulate in water is given by $p = 27{\cdot}58 + 0{\cdot}173t + 0{\cdot}0031t^2$ where p is g. of $Ca(C_5H_7O_3)_2,2H_2O$ in 100 g. of solution and t is temp. in °C. (Cox, Dodds, and Clasper, J. Amer. Pharm. Assoc. 1934, **23**, 662).

J. N. E. D.

ACETOPURPURINE 8 B. Disazo dye, from dichlorobenzidine and β-naphthylamine-3 : 6-disulphonic acid.

ACETOPYRINE. *Acopyrin. Pyrosal. Phenazopyrine.* Trade names for antipyrine acetylsalicylate, m.p. 63°–65°. Analgesic, antiseptic.

ACETOSAL *v.* ASPIRIN.

ACETOXANE. *Acetozone. Neurodin.* Trade names for *p*-acetoxyphenylurethane, $EtO{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OAc$, m.p. 87°. Hypnotic.

ACETOZONE *v.* ACETOXANE.

ACETYLCHOLINE BROMIDE. *Pragmoline.* Acetyl-ethanol-trimethylammonium bromide, $CH_2(OAc)CH_2{\cdot}NMe_3Br$. It is used in the treatment of arterial hypertension.

ACETYLCHOLINE CHLORIDE, also a vasodilator.

ACETYLENE. Synopsis of the subject :—

I. General, p. 73.

II. Methods of Production.—(*a*) HISTORICAL AND GENERAL, p. 74. (*b*) FROM CALCIUM CARBIDE, p. 74. (*c*) BY DIRECT SYNTHESIS, p. 75. (*d*) PYROGENETIC METHODS, p. 75.

III. Physical Properties, p. 78.

IV. Chemical Properties.—(*a*) REDUCTION PRODUCTS, p. 79. (*b*) OXIDATION PRODUCTS, p. 80. (*c*) ACETIC ACID, p. 80. (*d*) ACETONE, p. 81. (*e*) METALLIC DERIVATIVES, p. 82. (*f*) HALOGEN DERIVATIVES, p. 82 (for *chlorine derivatives, see article* ACETYLENE, CHLORINE DERIVATIVES OF, p. 96). (*g*) MISCELLANEOUS REACTIONS, p. 83.

V. Polymerisation Reactions.—(*a*) PYROGENETIC CONDENSATIONS, p. 85. (*b*) CUPRENE, p. 87. (*c*) VINYL ACETYLENE, DIVINYL ACETYLENE, ETC., p. 87. (*d*) VINYL HALIDES AND ESTERS, ETC., p. 90.

VI. Methods of Analysis, p. 96.

Acetylene, C_2H_2, is the first member of the series of unsaturated aliphatic hydrocarbons to which it gives its name, of the general formula : C_nH_{2n-2}. This formula applies also, of course, to the dialkylenes, which are characterised by the presence of two double linkages whereas the acetylene hydrocarbons possess one triple linkage :

$CH{\vdots}CH$	$CH{\vdots}C{\cdot}CH_3$	$CH_3{\cdot}C{\vdots}C{\cdot}CH_3$
Acetylene (C_2H_2)	Propine, or Methylacetylene (C_3H_4)	Butine, or Dimethylacetylene (C_4H_6)

and $CH_2 : C : CH_2$ Propadiene (C_3H_4) $CH_2 : CH{\cdot}CH : CH_2$ Butadiene (C_4H_6)

The dialkylenes will not therefore be considered in this section ; for convenience also the acetylene homologues are dealt with separately (*see* BUTADIENE ; ISOPRENE ; SYNTHETIC RUBBER ; ACETYLENES). The important polymers of acetylene, such as vinyl-acetylene, $CH_2 : CH{\cdot}C{\vdots}CH$, and divinyl acetylene,

$$CH_2 : CH{\cdot}C{\vdots}C{\cdot}CH : CH_2,$$

are, however, discussed in the present article (*see* p. 87).

I. GENERAL.

Nomenclature.—The systematic name for acetylene is *ethine*, the ending *-ine* indicating a member of the acetylene series, thus propine, butine, etc. In practice, however, the original name acetylene is always used as being well established and unlikely to cause confusion. With the exception of methylacetylene and dimethylacetylene, which are termed *allylene* and *crotonylene* respectively, the higher members of the series are usually named as substituted acetylenes, *e.g.* phenylacetylene.

Historical.—The production of acetylene by the treatment with water of the impure residues obtained during the preparation of potassium was first observed by E. Davy (Brit. Ass. Report, 1836, p. 62 ; Annalen, 1837, **23**, 144). The properties of the gas were first examined by Berthelot, who determined its composition, described its main properties, and showed its production in many pyrochemical processes (Compt. rend. 1862, **54**, 640 ; Annalen, 1862, **123**, 212 ; Ann. Chim. Phys. 1901 [vii], **23**, 444 ; 1905 [viii], **6**, 182).

Wöhler in 1862 showed that acetylene was produced on treating calcium carbide with water (Annalen, 1862, **124**, 220), a discovery that proved some thirty years later to be the basis of the whole acetylene industry when Wilson, in 1892, demonstrated that calcium carbide could be readily manufactured from lime and coke in the electric furnace. For rather more than a decade after the introduction of calcium carbide on a commercial scale it was mainly of importance as a source of gas for illumination, as it was generally believed that the pure white light of acetylene and its ease of production from carbide would soon cause it to oust coal-gas to a great extent. This expectation has not been fulfilled, though acetylene continues to be of great use for various purposes, such as flares, etc.

The next stage in the development consisted in the use of the oxy-acetylene flame for the "autogenous welding" of iron and steel, an industry that to-day utilises a considerable amount of the gas, though limited by the competition of electric welding methods (*see* ACETYLENE, ITS USES IN INDUSTRY).

In the first decade of the present century attempts were made to effect the chemical utilisation of acetylene in different ways, chiefly by the addition of chlorine and the formation of various chlorine derivatives of suitable boiling-points, which can be used as solvents for many purposes and serve to replace inflammable materials such as benzene, gasoline, etc., for dry-cleaning, fat-extraction, etc.

From about 1910 to 1925 the main interest in acetylene centred in the fact that it has been found possible to utilise on a commercial scale the discovery originally made by Kutscherow in 1881 that acetaldehyde is readily formed on passing acetylene into diluted sulphuric acid containing a suitable mercury catalyst, and progress in this field has been remarkably rapid in recent years; the production of acetic acid, acetic anhydride, and acetone from acetylene is now a branch of chemical industry of considerable magnitude.

During the last decade (1925–35) there have been three main lines of development in connection with acetylene: (i) the production of cheap acetylene from hydrocarbon oils and gases from various sources by thermal treatment, *e.g.* in an electric arc; (ii) the production of vinyl esters and halides, and their polymerisation to plastic substances; (iii) the conversion of acetylene to vinyl-acetylene, $CH_2:CH{\cdot}C:CH$, thence to "chloroprene," $CH_2{\cdot}CHCl{\cdot}CH:CH_2$, and its polymerisation to "Duprene," which is perhaps the most successful synthetic rubber yet produced.

II. METHODS OF PRODUCTION.

(*a*) **Historical Methods.**—It is unnecessary to consider in detail here the various laboratory methods which have been devised for the production of acetylene and it will suffice to summarise the known methods shortly:

(1) *from ethylene dibromide or dichloride* by the action of alcoholic potash:

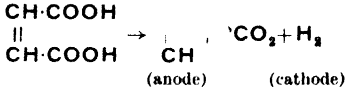
$$CH_2{\cdot}Br{\cdot}CH_2Br-HBr \rightarrow CH_2:CHBr$$
$$CH_2:CHBr-HBr \rightarrow CH:CH$$

(2) *from tetrachlorethane and metallic zinc*.

$$CHCl_2{\cdot}CHCl_2+4Zn=CH:CH+2ZnCl_2$$

Other alkyl halides, such as iodoform may be used, and silver [illegible]pper, etc., as reducing agents.

(3) *By electrolysis* [illegible] *or fumaric acids*:



$$\begin{array}{c}CH{\cdot}COOH\\ \|\\ CH{\cdot}COOH\end{array} \rightarrow \underset{\text{(anode)}}{\begin{array}{c} \\ |\\ CH\end{array}},\ \underset{\text{(cathode)}}{CO_2+H_2}$$

(4) *From acetylene mono- or dicarboxylic acids*:

$$C_2(COOH)_2=CH:CH+2CO_2$$

(5) *From propiolaldehyde and alkali*:

$$CH:C{\cdot}CHO+NaOH = CH:CH+H{\cdot}COONa$$

(6) *From copper acetylide* by the action of aqueous potassium cyanide (von Baeyer, Ber. 1885, **18**, 2273; Zeisel, Annalen, 1878, **191**, 368; Römer, Annalen, 1886, **233**, 182; Noyes and Tucker, Amer. Chem. J. 1897, **19**, 123). This method is stated to yield extremely pure acetylene; if hydrochloric acid be used instead of potassium cyanide, the gas is less pure and may contain traces of vinyl chloride.

(*b*) **From Calcium Carbide**, by the action of water:

$$CaC_2+H_2O=Ca(OH)_2+C_2H_2$$

Barium and strontium carbides behave similarly (Wöhler, Annalen, 1862, **124**, 220; Travers, Chem. Soc. Proc. 1893, 15; Maquenne, Compt. rend. 1892, **115**, 558; Moissan, Bull. Soc. chim. 1894 [iii], **11**, 1007; Lewes, J.S.C.I. 1897, **16**, 33; Clowes, *ibid.* **209**, 319; Wilson, *ibid.* 1896, **15**, 103; Lüpke, Elektr. Chem. Zeit. 1895, 145; Wyatt, J.S.C.I. 1895, **14**, 135, 796; 1901, **20**, 109; Bamberger, Z. angew. Chem. 1898, 720). This is by far the most convenient and practicable method for the production of acetylene and is at present almost invariably used for the technical production of the gas.

In the laboratory a convenient method for preparing acetylene is to cover calcium carbide with absolute alcohol and to add water dropwise (Matthews, J. Amer. Chem. Soc. 1899, **22**, 106). (For the technical production of acetylene and its use as an illuminant, *see* ACETYLENE, ITS USES IN INDUSTRY.)

Details as to British Patents dealing with the subject will be found in the Patent Office Abridgement Lists, Class 2 (1855–1909), Class 2 (i) (1910–1930), and Class IV (1931—and on).

Purification.—One of the chief objections to acetylene produced from calcium carbide is the fact that the various impurities (sulphur, phosphorus, etc.) present in the carbide produce the corresponding hydrides on treatment with water, thus contaminating the acetylene with small amounts of phosphine, hydrogen sulphide, ammonia, arsine, etc., in addition to traces of carbon monoxide, hydrogen, nitrogen, and oxygen. Phosphine is probably the most harmful impurity from the chemical and physiological point of view.

The method for producing odourless acetylene from carbide obtained from purified lime is too expensive to be practicable (Ide, Jap. Pat. 30209). In practice crude acetylene can be cleared of its active impurities by scrubbing with suitable liquids such as acidified copper sulphate solution, chromic acid dissolved in acetic or sulphuric acids, or with calcium, lead or mercury salts, or with bleaching powder. Sumiya and Yamada (J. Chem. Soc. Japan, 1930, **33**, 527 ; B. 1931, 467) have examined various commercial preparations for the purification of acetylene and recommend a "Heratol" type (*cf.* G.P. 116058) based upon bleaching powder, whilst the product of B.P. 181571 is also said to be satisfactory. Another type of "recoverable" purifier consists of a ferric salt on infusorial earth ; a recommended formula is : ferric chloride 9 parts, cupric acetate 0·6 parts, mercuric chloride 0·15 parts, ferric acetate 1·68 parts, deposited upon an infusorial earth (Sumiya and Yamada, *l.c.*).

Recent methods for the production of acetylene by pyrolysis of liquid or gaseous hydrocarbons yield products containing acetylene together with allylene, di-acetylene, etc., which must be removed before the acetylene is suitable for further treatment, whilst the acetylene itself may need to be concentrated. Thus, I.G. Farbenindustrie A.-G. purify such acetylene by washing the crude gases with concentrated sulphuric acid or by treatment with phosphoric acid, aluminium chloride, silica gel, etc., to polymerise and remove impurities ; alternatively the gases may be passed over catalysts such as the oxides of manganese, chromium, uranium, molybdenum, tin, etc., deposited on silica gel, at 200°–300°, or the gases may be scrubbed, for instance, with *cyclo*hexanone under pressure (B.P. 325817, 368782) ; or other solvents such as nitrobenzene, gas-oil, chlorinated solvents, etc., may be used (B.P. 386052). In B.P. 371142 the same inventors propose the addition of some methyl alcohol vapour to the crude gas followed by cooling first to −30° to remove moisture and impurities, and then to a lower temperature (*e.g.* −80°) to freeze out pure acetylene. The use of various glycols, polyglycols, or their ethers and esters as suitable solvents is claimed by the N. V. de Bataafsche Petroleum Maats., in B.P. 400054, and in this case the acetylene itself may be absorbed in the cooled solvent under pressure, the purified acetylene being recovered by releasing the pressure and warming the liquid (*cf. also* B.P. 331610).

Apart from actual purification, acetylene-rich mixtures may be concentrated by selective absorption, under pressure and at a low temperature, in alkyl carbonates such as diethyl carbonate, di-*n*-butyl carbonate, etc., the acetylene being recovered by heating the solution under reduced pressure (Metzger and Air Reduction Co., B.P. 401531 ; U.S.P. 1900655). A similar process is described (in U.S.P. 1938991) by Wulff, and consists in washing the acetylene-rich gas with hexane at −80° and fractionating the resulting solution.

Alternatively, acetylene-rich gases obtained by thermal methods may be purified from di-acetylene, etc., by passing them over a porous absorbent such as activated carbon or silica gel, followed, or preceded, by treatment with ferrous sulphate solution or alkali to remove cyanogen compounds (I.G. Farbenind. A.-G., B.P. 340787), whilst in B.P. 377193 the same firm proposes the removal of acetylene from gaseous mixtures by washing with such liquefied gases as sulphur dioxide, ammonia, carbon dioxide, methyl chloride, etc., at high pressures. The removal of small quantities of acetylene in hydrocarbon gases, where it is present mainly as an impurity, is dealt with in B.P. 359421–2 (I.G. Farbenind. A.-G.), in which the acetylene is either polymerised or destroyed.

Yet another method for purifying and concentrating diluted acetylene is that adopted by the Société de l'air liquide, which consists in dissolving acetylene in water under pressure and, after removal of the undissolved gases, extracting the acetylene by reduction of pressure (*cf.* B.P. 345237, 359279, 389946).

(*c*) **By Direct Synthesis.**—Acetylene is formed to a limited extent by the direct union of carbon and hydrogen in the electric arc :

$$2C + H_2 = C_2H_2$$

(Berthelot, Compt. rend. 1862, **54**, 640 ; Annalen, 1862, **123**, 212 ; Ann. Chim. Phys. 1901 [vii], **23**, **444** ; 1904 [viii], **6**, 182 ; Bone and Jordan, J.C.S., 1897, **71**, 41 ; 1901, **79**, 1042 ; Pring and Hutton, *ibid.* 1906, **89**, 1600 ; v. Wartenberg, Z. anorg. Chem. 1907, **52**, 310). This method is, however, almost entirely of academic and historical interest.

(*d*) **Pyrogenetic Methods.**—Although the production of acetylene by the action of water on calcium carbide is still the standard method, it has been found in recent years that on passing hydrocarbon gases rapidly through an electric arc or an oxygen-fed flame and cooling the products quickly, a good yield of acetylene is obtainable. Alternatively, by forming an A.C. arc in heavy oil a gas is evolved consisting mainly of hydrogen and acetylene, which may be suitably separated, or the acetylene may be utilised to form acetaldehyde or other products. Various individuals and firms have taken out numerous patents on these lines.

The problem has been examined on the theoretical side by various workers, notably F. Fischer and his students : *e.g.* Fischer, Pichler, Meyer, and Koch (Brennstoff-Chem. 1928, **9**, 309) ; Fischer and Peters (*ibid.* 1929, **10**, 108 ; Z. physikal. Chem. 1929, **141**, 180) ; Fischer, Bangert, and Pichler (Brennstoff-Chem. 1929, **10**, 279) ; Peters and Meyer (*ibid.* 324) ; Fischer, Peters, and Koch, *ibid.* 383 ; Peters and Prauschke (*ibid.* 1930, **11**, 239) ; Fischer and Pichler (*ibid.* 501) ; Fröhlich, White, and Dayton (Ind. Eng. Chem. 1930, **22**, 20) ; de Rudder and Biedermann (Compt. rend. 1930, **190**, 1194) ; Peters and Wagner (Z. physikal. Chem. 1931, **153**, 161) ; Fischer and Peters (Brennstoff Chem. 1931, **12**, 268) ; Smith, Hawk, and Reynolds (Ind. Eng. Chem. 1928, **20**, 1341) ; Rudder and Biedermann (Bull. Soc. chim. 1930, **47**, 710) ; Storch (Bureau of Mines Circular 6549 (1932) ; J. Amer. Chem. Soc. 1932, **54**, 4188); Storch and Golden (*ibid.* 1932, **54**, 4662); Kassel (*ibid.* 1932, **54**, 3949); Hawk, Golden, Storch, and Fieldner (Ind. Eng. Chem. 1932, **24**, 23); Storch and Golden (*ibid.* 1933, **25**, 768); Storch (*ibid.* 1934, **26**, 56); Fischer and Pichler (Brennstoff-Chem. 1932, **13**, 381, 406, 441).

Peters and Wagner (*l.c.*) examined the behaviour of methane in presence of varying amounts of hydrogen when exposed to a high-tension arc under reduced pressure, the most suitable proportions being $\frac{2}{3}$ methane (by volume) and $\frac{1}{3}$ hydrogen. By working at 15–20 mm., methane may be converted almost completely into acetylene, but it is preferable to use a diluted gas such as coke-oven gas, in which case the optimum yields were obtained at 40–50 mm. The optimum yield of acetylene was obtainable by working at as high a temperature and as low a pressure as were practicable. Storch (Ind. Eng. Chem. 1934, **26**, 56) has reviewed the industrial possibilities of acetylene production by the controlled pyrolysis of hydrocarbons.

Fischer and Pichler (Brennstoff-Chem. 1932, **13**, 406) obtained up to 90% conversion of ethylene to acetylene by heating a mixture of ethylene (which may contain hydrogen) and methane to 1300°-1400° at 0·1 atm. for a very short time; with longer heating liquid polymerides were obtained. The same investigators by passing a stream of methane through a heated tube at 1300°, for about 0·016 second contact, obtained 76 g. acetylene per cubic metre of methane together with about 60 g. of light oil, but above 1400° only acetylene was obtained, whilst by working at 50–70 mm. pressure a 70–80% yield of acetylene was claimed, and a coke-oven gas containing 25% of methane gave a 75% conversion of methane to acetylene (*ibid.* p. 381).

Montagne (Compt. rend. 1932, **194**, 1490) has shown that by condensed sparking of methane at 1 to 11 mm. pressure the main reaction is $2CH_4 \quad C_2H_2+3H_2$, whilst Balandin, Eidus, and Zalogin have examined the formation of acetylene by submitting ethylene to a high-frequency discharge (Compt. rend. Acad. Sci. U.R.S.S. 1934, **4**, 132; A. 1935, 192). The production of acetylene from coke-oven gases is discussed by Osterreith (J. Inst. Fuel, 1933, **6**, 215). Peters and Meyer (Brennstoff-Chem. 1929, **10**, 324) by varying the conditions of reaction, found that the yield of acetylene from methane increased to a maximum at the highest attainable temperature under reduced pressure, whilst the formation of oily products was prevented.

The intense activity in this field of industrial chemistry is due not only to the possibility of utilising the large volumes of methane produced from coke and by-product ovens, which at present serve merely as gaseous fuel, but is also owing to the close connection with problems of coal hydrogenation and the production of liquid fuels. The following further recent patents may be noted:

I.G. Farbenindustrie A.-G.—The efficiency of the process is greatly increased by the preliminary removal of all carbon monoxide present (B.P. 306008); the production of ethylene and acetylene by the rapid passage of saturated aliphatic hydrocarbons, such as methane, at 700°–1000°, over a contact-mass consisting of alkaline-earth metal salts, or of salts, oxides or hydroxides of magnesium or beryllium, compounds of selenium, tellurium, thallium, activated silica or activated charcoal is referred to in B.P. 264827; acetylene is the main product at high temperatures and ethylene at lower temperatures. In B.P. 264845 the same inventors describe a form of apparatus in which methane, etc., is thermally decomposed by rapid passage through a disc-like flame extending across the whole cross-sectional area of a tube; the products may be either rapidly cooled to separate the hydrocarbons, or subjected to further treatment to yield benzene or acetaldehyde. In B.P. 265234 (void), I.G. Farbenindustrie A.-G. describe methods for effecting the conversion of methane into acetylene: methane pre-heated to 900°C. is passed through a quartz tube in which is a flame-zone fed by four nozzles delivering oxygen, affording a temperature of over 1000°. In a modification, methane is passed through an iron tube lined with refractory material over part of its length, oxygen being introduced through nozzles. The same patentees also pass a mixture of 20% methane and 80% hydrogen through an electric arc, the resultant acetylene being adsorbed on active charcoal; alternatively, natural gas is subjected to incomplete combustion and the product, containing acetylene, is passed at 700° over silica coated with graphite, to yield benzene (B.P. 269547).

Methane, ethane, ethylene, etc., may be converted into acetylene by pyrogenic treatment in an electric arc using superimposed high- and low-frequency currents, in presence of catalysts, such as iron, nickel, or cobalt, or lustrous carbon (B.P. 320362). By increasing the rate of flow unsaturated hydrocarbons are obtained, mainly consisting of higher olefines or di-olefines (B.P. 315249). The gases obtained during the destructive hydrogenation of coal are passed through an electric arc, and the gases, now containing 8% of acetylene, are passed at 20 atm. through active charcoal to adsorb the acetylene (B.P. 325309). A mixture of methane (3 vols.) and hydrogen (1 vol.) is passed through a sequence of electric arcs, the acetylene formed being removed at each stage (B.P. 337088). Acetylene is formed by passing gaseous mixtures containing at least 20% of methane through a Schönherr type of electric furnace; the ratio of gas (cu. m.) to current consumption (kw.) lies preferably between 0·6 and 1·6 (B.P. 332917). A similar process is covered by B.P. 389165, in which part of the gas supplied is introduced tangentially to impart a rapid movement to the striking point of the arc in order to avoid the deposition of carbon; by this process a gas containing 95% of propane yields a product containing 14% to 16% of acetylene.

In B.P. 354735 a type of apparatus is described for subjecting methane to electric discharges to produce acetylene: using a gas containing 30% of methane, at a rate of flow of 200 metres per second, a 10% yield of acetylene is claimed. I.G. Farbenindustrie A.-G. claim, in B.P. 336261, the manufacture of carbon black, acetylene, and hydrogen, by passing methane or natural gas through an electric arc at such a rate that the ratio of the number of cu. m. of gas passed through the arc per hour to the power of the arc in kw. lies below 0·6. In B.P. 365045 acetylene is prepared from paraffin hydrocarbons by treatment in an electric arc generated by an A.C. current of not more than 500 cycles, under such conditions that the decrease from the "no-load" tension to the working tension is more than 30%. Yields of acetylene up to 16% may be obtained by passing finely dispersed liquid or gaseous hydrocarbons through a tubular electric furnace in which the electric arc therein has a minimum energy consumption of 2 kw./sec./cc. of space (B.P. 370414). In B.P. 371916–7 hydrocarbon gases are passed through a water-cooled electric furnace and then into a large cooled separating chamber to remove carbon black, the gas being cooled in two or more stages on a series of water-cooled surfaces. The use of a fine suspension of inert matter (such as sand or ashes) in the electric furnace is claimed to prevent the deposition of solid deposit in the arc space (B.P. 382690). In B.P. 397987 hydrocarbon gases are passed consecutively through two or more electric arcs of increasing power, so that the concentration of acetylene increases during the passage of the gas.

Methods for attaining suitable high temperatures for pyrolysis by partial combustion of hydrocarbons are claimed in the following patents: suitable hydrocarbons together with small amounts of air or oxygen are passed over silicon at 700° to 1100° at 0·5 to 5·0 atm. (B.P. 347493). Methane or its homologues are heated to such a temperature that not less than 5% of the hydrocarbons are converted into olefines, and the resulting gases are then submitted to partial combustion at temperatures above 1000°C. to produce acetylene (B.P. 408691, 408934).

In B.P. 363375 a mixture of methane, carbon monoxide, and hydrogen obtained by partial combustion of methane, heated to 500°–700° is passed rapidly through an electric arc, quickly cooled, the carbon removed, and the residual gases recirculated.

A mixture of 90% propane and butane with nitrogen, hydrogen, carbon dioxide, and methane yields acetylene when partially burnt in air in contact with a cylinder of compressed silicon heated electrically to 900°C. (B.P. 347493). (*See also* B.P. 318270, 382690.)

Imperial Chemical Industries, Ltd.—Ethylene is heated to 1100°C. at a space velocity of 6,400 reciprocal minutes, 30% of the gas being obtained as a light oil and 8% as acetylene (Wheeler, McAulay, and I.C.I., Ltd., B.P. 332998). Gaseous or vaporised hydrocarbons, other than methane, mixed with steam, are heated to temperatures above 1000°C. for less than 2 seconds to produce acetylene (Ferguson and I.C.I., Ltd., B.P. 342771). Acetylene is formed by pyrolysis of methane and its homologues above 1000°C. in presence of at least an equal volume of a gaseous diluent, other than steam (Binnie and I.C.I., Ltd., B.P. 343881). Ethane, propane, etc., are heated at 1200° or over, for 50, 100, or even several thousand reciprocal minutes to produce acetylene, ethylene, benzene, etc. (McAulay, Francis, Wheeler, and I.C.I., Ltd., B.P. 342359). The heat necessary for converting methane into acetylene may be provided by the combination of chlorine and hydrogen in a constricted space (Binnie, Wheeler, and I.C.I., Ltd., B.P. 353913). The acetylene formed in such thermal processes may be recovered from gaseous mixtures by countercurrent washing with glycol diacetate at 10°C. and 6 atm., the residual gas being compressed to 50 atm. and again submitted to treatment (Hull and I.C.I., Ltd., B.P. 331610). (*Cf. also* B.P. 400054.)

Of other processes the following may be noted: Gross illustrates an apparatus in which a mixture of ethylene hydrocarbons and methane is converted into acetylene and hydrogen by submitting it to a spark discharge (G.P. 434831). (*See also* B.P. 390492, Fischer and Pichler.) Other electrical processes are those of Brading (U.S.P. 1797400), consisting in passing finely divided carbon together with pre-heated hydrogen through an electric arc; the preparation of acetylene from methane or a mixture of methane and hydrogen by the action of A.C. discharges (Institut für phys. Grundlagen der Medizin, B.P. 362869); the process of Kipper and Knox (U.S.P. 1883799), in which petroleum oil is injected by means of a current of hydrogen into an electric arc formed between a stationary and a rotating conical electrode, the gaseous products being rapidly withdrawn. In B.P. 368164 the Soc. Chem. Industry in Basle claim the production of acetylene from hydrocarbons by circulating the gases continuously *via* tubular electrodes through an electric arc in which the current density of at least one of the electrodes is raised to the point at which loss of substance can be detected. The Société de l'Air Liquide in B.P. 377358 (void) obtain a mixture of acetylene, hydrogen, and carbon monoxide by passing gaseous hydrocarbons containing methane, admixed with steam and/or oxygen, through an electric arc.

Of alternative methods involving partial combustion to provide the necessary heating effect, Millar and the Shell Development Co. propose the use of an "inverted flame," *i.e.* burning oxygen or air in natural gas or oil (U.S.P. 1896552); whilst Burgin, Groll, and the Shell Development Co. in U.S.P. 1965770, obtain acetylene by the partial combustion of hydrocarbon gases, such as natural gas, at temperatures above 850°, with less than half the amount of oxygen necessary for complete combustion. The gas velocity is maintained greater than the flame velocity of the mixture and combustion is maintained by the use of separate pilot flames.

Wulff, in a series of patents, claims (i) heating hydrocarbons for less than 5 seconds to a high temperature above 980°, together with chlorine or sulphur and steam (U.S.P. 1880310); (ii) a reaction chamber packed with carborundum particles is heated above 1400° by the combustion of fuel gas and air, natural gas is passed through the chamber, and the issuing gas, which contains 5–6% of acetylene, is rapidly cooled (U.S.P. 1917627) ; (iii) in an ingenious method described in U.S.P. 1880307 and 1966779 Wulff claims the production of acetylene by sudden compression of pre-heated natural gas or "cracked" gas to about 50 atmospheres so as to obtain momentary temperatures of 1370° or over, the pressure being then rapidly released in order to cool the product by expansion (*cf. also* Wulff, B.P. 334178).

Mixtures containing acetylene, carbon monoxide, and hydrogen are formed by rapidly heating saturated hydrocarbons with steam and oxygen to 1300° or higher (Société d'Études Scientifiques, B.P. 349067 ; 352280). Hydrocarbons are degraded to acetylene by passing through an "inverted" oxygen-fed flame (B.P. 364418), or propylene may be converted into acetylene by heating for a short time to 700°–800° (N. V. de Bataafsche Petroleum Maatschappig, B.P. 369351). In B.P. 391206, Ruhrchemie A.-G. obtain acetylene from methane by heating the gas in a regenerative system, under reduced pressure. The Soc. Ind. des Hydrocarbures & Dérivés obtain acetylene from methane, using a halogen compound as a catalyst, by heating the gas to 950°–2000°C., under reduced pressure, the duration of heating diminishing from 15 secs. at 1000° to 0·01 sec. at 1500°, the products being withdrawn continuously (B.P. 352688). Lastly, Banck (U.S.P. 1773611) obtains a mixture of acetylene and hydrogen by passing a pre-heated mixture of methane and an inert gas, under reduced pressure, over a large surface of porous carbon heated electrically to 1400°–2000°C. (*cf. also* Knapp, U.S.P. 1023783).

Whilst little is known as to the extent to which such processes for the commercial production of acetylene may be utilised industrially it is obvious that the method of preparing the gas by thermal processes is regarded as being of major importance. Some information has been published regarding one electrical process (L'Air Liquide, Soc. anon. pour l'étude et l'exploitation des procédés G. Claude) (*cf.* B.P. 345237, 359279, 389946), in which an electric furnace is used, containing two hollow graphite electrodes. Crude oil is circulated through an earthed electrode and an arc is formed between this and the second, insulated, electrode. The gases formed, together with unchanged oil, are conveyed from the furnace to a condensing system where the oil is recovered, filtered, and returned to the circulatory system. The arc works at a tension of 1000 volts D.C. and is maintained by means of a special high-frequency pilot arc discharging at 30,000 volts through a condenser, at 1000 periods per second. The current consumption on a semi-scale plant amounts to about 3·5 kw.h. per cubic metre of gas produced, containing 35% of acetylene, or, allowing for an efficiency of the furnace of 85%, the total consumption would be 4·1 kw. per cu. m. of gas.

The crude gas is separated by extraction with water under 10 atm. pressure to yield a product containing 85% of acetylene, which is raised to 99% by a second extraction with water at 5 atm.

A typical semi-scale flow sheet gives the following figures ; for the production of 1 cu. m. of 99% acetylene (=1·13 kg.) per hour, there are required :

Oil (including losses) . .	2·2 kg.
Electrical energy (furnace, etc.)	14·0 kw.h.
Electrical energy (pumps, etc.)	1·5 kw.h.
Graphite electrodes . .	3 to 4 g.

As by-products there are obtained about 0·500 kg. carbon black and 3·8 cu. m. of a gas containing 75% of hydrogen.

III. Physical Properties.

Acetylene is a colourless gas having a pleasant ethereal odour in a pure state, which is, however, usually disguised by the presence of fœtid-smelling impurities. In liquid air it solidifies to a crystalline mass which can be burnt like a candle. Its melting-point, variously given as −81°C. (Ladenburg and Krügel, Ber. 1899, **32**, 1821 ; 1900, **33**, 638 ; Hunter, Chem. Zentr. 1906, ii, 485) ; −81·5° (McIntosh, J. Physical Chem. 1907, **11**, 306 ; Maass and McIntosh, J. Amer. Chem. Soc. 1914, **36**, 737), is above its boiling-point at ordinary pressures :−82·4° (Ladenburg and Krügel, *l.c.* ; Hunter, *l.c.*) ; −88·5° (McIntosh and Maass, *l.c.*) ; −83·9° (Burrell and Robertson, J. Amer. Chem. Soc. 1915, **37**, 2482). Sublimation point, −83·6° (Maass and McIntosh, *l.c.*). Critical temperature 37·05° (Ansdell, Proc. Roy. Soc. 1879, **29**, 209 ; Heilborn, Z. physikal. Chem. 1891, **7**, 604) or 36·5° (McIntosh, *l.c.*). Critical pressure 61·6 atm. (McIntosh, *l.c.*) and critical volume 83 c.c. (McIntosh, *l.c.*). Cardoso and Baume give critical temperature 35·5°, and critical pressure 61·5 atm. (Compt. rend. 1910, **151**, 141). For other physical constants, *see* McIntosh (*l.c.*) ; also Morehouse and Maass, Canad. J. Res. 1934, **11**, 637.

Liquid acetylene is a mobile fluid, d^{0} 0·451 (Cailletet, Compt. rend. 1877, **85**, 851 ; Ansdell, Jahresber. d. Chem. 1879, 68) or d^{-75} 0·73 (McIntosh, *l.c.*). It has a high electrical resistance which is not appreciably altered by the addition of alcohol, ether, halogen hydride, etc. (McIntosh, *l.c.*).

Acetylene is readily soluble in many organic solvents, forming crystalline compounds (McIntosh, *l.c.*) ; thus, at 18° chloroform and benzene absorb about four times their volume, acetic acid and alcohol about six times their volume ; it is also appreciably soluble in water, glycol ethers, and esters, etc., the solubility increasing under pressure ; this property is utilised for the extraction and purification of the crude gas, as noted above (*see* p. 75). It is extremely soluble in acetone, which absorbs 25 times its volume of the gas at 15°C. and 760 mm. ; under 12 atm. it takes up 300 volumes, whilst at −80° acetone absorbs more than 2000 volumes of acetylene (Claude and Hess, Compt. rend. 1897, **124**, 626 ; Claude, Compt. rend. 1899, **128**, 303). This property of acetone is of great technical importance for the storage of dissolved acetylene for illuminating purposes and in acetylene welding (*see* Acetylene, its Uses in Industry). The solubility in water is about 1% by volume at 12°C., but increases considerably with pressure and cooling ; it forms a hydrate, $C_2H_2+6H_2O$. The solubility is lowered by the addition of salt (Claude and Hess, *l.c.*). Acetaldehyde dissolves half its weight of acetylene and its use as a solvent has been suggested (James and Watson, U.S.P. 92887 ; James, Ind. Eng. Chem. 1913, **5**, 115). The solvent power of organic solvents for acetylene appears to be associated with the presence of a carbonyl group and with low molecular weight.

Acetylene is an endothermic compound, the heat of formation from its elements being approximately 50 kg.-cal. As a consequence both the gas and the liquid are highly explosive, particularly under pressure, for which reason solvents are used for storage. The explosive properties of acetylene have been discussed by de Liefde (Chem. Weekblad, 1934, **31**, 711 ; B. 1935, 835). The molecular heat of combustion is 312·9 kg.-cal. at constant pressure. The specific heat and dissociation of acetylene are discussed by Ruedy in Canad. J. Res. 1932, **7**, 328.

For the optical properties of the gas the following papers may be referred to : absorption spectrum, Jonesco, Compt. rend. 1934, **199**, 710 ; ultra-violet absorption spectra, Kistiakowsky, Physical Rev. 1931 [ii], **37**, 276 ; Herzberg, Trans. Faraday Soc. 1931, **27**, 378 ; infra-red absorption spectra, Badger, Physical Rev. 1930 [ii], **35**, 1433 ; Eastwood and Lochte-Holtgreven, Nature, 1932, **130**, 403 ; Sutherland, Physical Rev. 1933 [ii], **43**, 883 ; mass spectrum of acetylene and products of ionisation, Tate, Smith, and Vaughan, *ibid.* 1933 [ii], **43**, 1054 ; Raman effect, Glockler and Davies, J. Chem. Phys. 1934, **2**, 881 ; spectra of "heavy" acetylene, *v. infra*, Sutherland, Nature, 1934, **134**, 775 ; Herzberg, Patat, and Spinks, Nature, 1934, **133**, 951 ; Randall and Barker, Physical Rev. 1934 [ii], **45**, 124.

Acetylene, when pure, has no action upon metals at normal temperatures, but industrial acetylene readily attacks copper owing to the presence of impurities which facilitate the formation of the explosive copper acetylide (Reckleben and Scheiber, Chem.-Ztg. 1915, **39**, 42 ; 1916, **40**, 325). Nickel and tin are little attacked by acetylene and it is suggested by Reckleben and Scheiber that metals exposed to the action of acetylene should be coated with one of these metals. It is non-poisonous in small quantities but may produce asphyxiation if more than 40% is present, and is used in surgery as a general anæsthetic under the name of *Narcylen*, but owing to its explosive nature it requires special care in its use. Anæsthesia is initiated at a 60% concentration and continued with 25% to 30%, the characteristic odour being masked by the use of an essential oil. Its use is especially recommended in childbirth (*cf.* Wieland and Gauss, Klin. Wochenschrift, 1923, **2**, 113 ; Horwitz, Lancet, 1923, i, 619 ; Haselhorst, Deut. med. Woch. **50**, 906 ; Philipp, Münch. med. Woch. **71**, 639). The purification of acetylene for anæsthetic purposes is claimed by Boehringer and Wieland, B.P. App. (1923), 20241.

Heavy Acetylene.—Reyerson and Yuster have shown that with acetylene and an 18·5% solution of D_2O no exchange occurs between hydrogen and deuterium in presence of H_3PO_4, but does so in presence of caustic soda (J. Amer. Chem. Soc. 1934, **56**, 1426). Klemenc and Frugnoni have investigated the vapour pressure of "heavy acetylene" between −110° and 85 (Naturwiss. 1934, **22**, 465).

The *structure* of acetylene is discussed by (Mrs.) E. H. Ingold (J.C.S. 1924, **125**, 1529).

IV. Chemical Properties.

(*a*) **Reduction Products.**—Owing to its unsaturated nature acetylene readily enters into reactions to form addition products. Thus it adds on hydrogen to form ethylene and ethane :

$$C_2H_2+H_2=C_2H_4$$
$$C_2H_2+2H_2=C_2H_6$$

This process is most effectively performed with the aid of nascent hydrogen in presence of a catalyst ; Lane (B.P. 10724, 1911) claims the synthesis of ethylene from acetylene and hydrogen by passing them over a heated catalyst contained in a series of tubes (*cf. also* Atterbury, B.P. 2961, 1898 ; Wideen, B.P. 9340, 1903 ; Bouchard-Praceiq, B.P. 6075, 1905). Kars (G.P. 253160) claims the production of ethylene from acetylene and hydrogen, using as a catalyst a mixture of at least one metal of the palladium or platinum group, with at least one of the following metals : iron, nickel, cobalt, copper, silver, magnesium, zinc, cadmium or aluminium. Eldred and Mersereau (U.S.P. 1308777) also put forward similar claims, the catalyst used being nickel or palladium on a carrier of coke, asbestos, pumice, etc. ; to prevent the action from becoming too vigorous the gas mixture is diluted with ⅓ to ½ of its volume of carbon dioxide or ethane. Yoshikawa also states that a nearly quantitative conversion of acetylene to ethylene may be effected by passing a mixture of acetylene and hydrogen over nickel or palladium distributed over kieselguhr (Bull. Chem. Soc. Japan, 1932, **7**, 201 ; *cf.* B.P. 294787, *infra*).

Acetylene is readily reduced to ethylene and ethane by means of hydrogen in presence of colloidal platinum or palladium ; in presence of palladium practically pure ethylene can be obtained if the metal is previously saturated with acetylene ; in presence of platinum 35–40% of ethane is produced simultaneously (Ber. 1910, **43**, 2684, 2692 ; Paal and Schwartz, 1915, **48**, 275, 1195, 1202 ; Paal and Hohenegger, 1913, **46**, 128 ; Chem.-Ztg. 1912, **36**, 60. *See also* Sabatier and Senderens, Compt. rend. 1900, **130**, 1559, 1628, 1761 ; **131**, 40, 187, 267 ; Bull. Soc. chim. 1901 [iii], **25**, 678 ; Salkind, Vishnjakov and Morev, J. Gen. Chem. Russ. 1933, **3**, 91 ; Salkind, Teterin, and Ivanova, *ibid.* 1933, **3**, 373).

Acetylene may also be reduced directly to ethylene by means of an aqueous solution of chromous chloride ; the same result is obtained if zinc dust, dilute hydrochloric acid, and a small quantity of chromous chloride be used. No ethane appears to be produced under such conditions (Traube and Passarge, Ber. 1916, **49**, 1692). The reaction may also be carried out under pressure (G.P. 287585 ; U.S.P. 1179051).

When acetylene and hydrogen (under varying conditions of pressure) are passed over various metallic catalysts such as finely reduced nickel, copper, cobalt or iron at moderately elevated temperatures, in addition to ethylene and ethane, liquid hydrocarbons are formed, *e.g.* copper or nickel yields a greenish hydrocarbon $(C_7H_8)_n$, termed *Cuprene* (*q.v.*, p. 87) (Sabatier and Senderens, Compt. rend. 1899, **128**, 1173 ; 1900, **130**, 250, 1559, 1628 ; 1900, **131**, 187 ; Erdmann and Köthner, Z. angew. Chem. 1905, **18**, 49 ; Gooch and Baldwin, *ibid.* 1909, **22**, 235 ; Petrov and Antzus, Compt. rend. Acad. Sci. U.R.S.S. 1934, **4**, 295 ; A. 1935, 325). By passing acetylene over the kathode of alkaline lye undergoing electrolysis, ethylene and ethane are formed (Billitzer, Monatsh. 1902, **23**, 199).

Ethylene may also be prepared by passing a mixture of acetylene and hydrogen in fine bubbles into an inert liquid, such as decahydronaphthalene, containing a suspension of palladium or nickel on kieselguhr, preferably at about 150° and under pressure (I.G. Farbenind. A.-G., B.P. 294787) ; or an acetylene-hydrogen mixture containing 5–20% of water vapour may be passed over aluminium powder, cerium or ceria at 280°–320°, preferably at normal pressure (B.P. 325695) ; the use of a catalyst of compact tellurium at 450° or sheet nickel at 180° minimises the production of ethane even with excess of hydrogen (B.P. 336999). The ethylene so obtained may be absorbed in concentrated sulphuric acid and the resultant ethyl sulphuric acid hydrolysed to alcohol (*cf.* B.P. 273263). Using a nickel mercury catalyst acetylene is reduced by hydrogen at 25°–30° to a light oil containing ethylene hydrocarbons, and a heavier oil.

(*b*) **Oxidation Products.**—A number of investigations have been made upon the oxidation of acetylene under various conditions ; thus Kistakowsky and Lenher (J. Amer. Chem. Soc. 1930, **52**, 3785) have examined the oxidation of acetylene by air in "Pyrex" glass tubes at 230°–315°C., and conclude that the reaction proceeds according to the scheme: acetylene → glyoxal → formaldehyde → formic acid, the gaseous products consisting mainly of carbon monoxide from direct decomposition of glyoxal, carbon dioxide from the formic acid, and hydrogen. Under suitable conditions the intermediate reaction products may be isolated (*cf.* Kistakowsky, *ibid.* 1930, **52**, 4837 ; Lenher, Kistakowsky, and Du Pont de Nemours, Ltd., U.S.P. 1955885).

Acetylene explodes violently with ozone, but by suitably moderating the reaction by diluting the mixture with air, hydrogen or carbon dioxide, and water-vapour, *glyoxal* may be obtained (Marks and Boshard, B.P. 140478).

The mechanism of the slow combustion of acetylene has been investigated by Spence (Nature, 1931, **128**, 153 ; J.C.S. 1932, 686), and points to a branched chain mechanism for the reaction. On exposing a mixture of acetylene and oxygen, saturated with moisture, to a "hot" quartz mercury arc, oxalic acid is formed (Livingston, J. Amer. Chem. Soc. 1931, **53**, 3909) ; whilst oxidation of acetylene at 0° with dilute permanganate yields mainly formic acid (Krestinski and Kelbovskaya, Ber. 1934, **68** [B], 512).

· Acetylene forms highly explosive mixtures with oxygen or air in any proportion from 3–82%, but the explosiveness is reduced by admixture with inert gases (Meyer, Ber. 1894, **27**, 2764 ; Le Chatelier, Compt. rend. 1895, **121**, 1144 ; Gréhaut, *ibid.* 1896, **122**, 832 ; Berthelot and Vielle, *ibid.* 1896, **123**, 523 ; Bone and Cain, Chem. Soc. Proc. 1896, 176 ; Clowes, J.S.C.I. 1896, **15**, 90, 418, 701, 891 ; Bundt, Ber. 1898, **31**, 5 ; Clowes, Chem. Soc. Proc. 1896, 413 ; Berthelot and Vielle, Compt. rend. 1899, **128**, 177 ; *cf. also* Delépine, 8th Intern. Congr. Appl. Chem. 4, 25, and J. Gasbel, **57**, 65). Amongst recent investigations may be noted those of Rossichin and Timkovski on the influence of high-frequency electrical fields on the combustion of an acetylene-air mixture (Nature, 1935, **135**, 916) ; flame temperatures of mixtures of methane and acetylene (Jones, Lewis, and Seaman, J. Amer. Chem. Soc. 1931, **53**, 3992) ; the reaction between acetylene and oxygen in presence of 1·7–4·0% nitric acid at 170°–250°, leading to the conversion of 50–60% of the gas to trimeric glyoxal (Lenher, J. Amer. Chem. Soc. 1931, **53**, 2692). Yagi and Takioka (J. Soc. Chem. Ind. Japan, 1931, **34**, 205) have investigated the explosion limits of crude acetylene admixed with air and state that there is no risk of explosion when the oxygen content is less than 8% and the acetylene content less than 2·5%. Bone, Frazer, and Lake (Proc. Roy. Soc. 1931, A., **131**, 1) have investigated the explosion products of mixtures of acetylene and electrolytic gas. The observation of Bone and Drugman (J.C.S. 1906, **89**, 669) that the reaction follows the course :

$$C_2H_2+O_2+2H_2=2CO+3H_2$$

was confirmed.

The explosibility of acetylene-steam mixtures has been examined by Rimarski and others (Jahresber. Chem. Tech. Reichs-amt. 1930, **8**, 43 ; A. 1931, 1015) : mixtures of C_2H_2+steam did not explode at ratios of 10 : 1 or 1 : 1·5 at 5–6 atm. but explosion occurred at a ratio of 1·63 : 1. Lauer (Z. Physik, 1933, **82**, 179) has made a spectroscopic study of the explosion zone of acetylene and air.

(*c*) **Acetic Acid.**—In the past much research has been directed towards the production of acetic acid by direct oxidation of acetylene. At the present day the problem has been completely solved technically by the less direct method of catalytic hydration to acetaldehyde (*q.v.*) in presence of mercury salts, with subsequent oxidation to acetic acid. The following processes indicate, however, that the commercial possibilities of direct oxidation of acetylene to acetic acid are still to be reckoned with : alkali metal acetates may be obtained from acetylene and steam by reaction with fused alkali hydroxides at 200°–350°C. (Dow Chemical Co., B.P. 363948 ; *cf. also* Feuchter, Ber. 1900, **33**, 2015) ; or acetylene and steam may be passed over a bismuth phosphate (or molybdate) catalyst at 300°C., to produce acetaldehyde and acetic acid (Tanner and Imperial Chem. Industries, Ltd., B.P. 344638). Acetic acid and aldehyde are obtained by passing a mixture of acetylene, air and a little nitric oxide over heated quartz or porcelain at 300°–400°C. (Gutehoffnungshütte Oberhausen A.-G., B.P. 376045), or a mixture of acetylene and steam may be passed through molten zinc chloride at 300°–450°C. (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 373893). The accelerating effect of a concentrated electromagnetic field upon the reaction between acetylene, steam, and ozone, to produce acetic acid, is referred to in B.P. 417501 (Ternion A.-G.). Hydrogen peroxide also converts acetylene into acetic acid (Cross, Bevan, and Heiberg, Ber. 1900, **33**, 2015). In U.S.P. 1128780 and F.P. 467515 (Farbwerke vorm. Fr. Bayer) a process is claimed for producing acetic acid by treating acetylene with a mixture formed from mercuric oxide, hydrogen peroxide, and ammonium or potassium persulphate in 10–30% sulphuric acid ; it is stated that 10·8 g. acetylene yield 24–25 g. acetic acid. An electrolytic process is described in F.P. 467778 (G.P. 293011 ; U.S.P. 1159376) consisting in oxidising acetylene at a platinum anode in a divided cell containing 30% sulphuric acid and 1–2% mercury salt, at 30°–40°C., with a lead or copper cathode, using a flow of 48·5 g. acetylene per hour and 100 amp., the yield is 0·5 kg. per 24 hours. Kárpáti and Hübsch pass acetylene and oxygen into glacial acetic acid containing a mercury salt and cellulose fibres, or superficially carbonised sawdust, cellulose acetate, colloidal lead peroxide, etc., preferably in a circulatory system (B.P. 287135, 294226).

An earlier patent of the Chem. Fabrik Griesheim-Elektron (B.P. 14113, 1914 ; Swiss P. 70152) claims the production of acetic acid by passing acetylene and oxygen, alternately or simultaneously, into acetic or other organic acid to which a suitable mercury catalyst has been added. It does not appear, however, to offer any advantage over the very successful method, now generally adopted, of oxidising acetaldehyde in presence of a manganese catalyst, and is therefore now mainly of historic interest. (*See* ACETIC ACID.)

For a discussion of the chemistry of the reactions involved in the conversion of acetaldehyde to acetic acid, *see* ACETALDEHYDE, p. 22.

(*d*) **Acetone.**—Numerous attempts have been made to prepare acetone directly from acetylene, although it does not appear that any of these have attained industrial success, especially in view of the fact that the direct methods of obtaining acetone either by passing acetic acid vapour over heated lime or from ethyl alcohol by passage over a red-hot iron-oxide-lime catalyst are now so satisfactory and well-established. The following examples may, however, be given : acetylene and steam are passed at 350°–450° over a catalyst such as potassium-thorium carbonate, mounted on burnt clay or pumice, with production of acetone (Elektrizitätswerk Lonza, B.P. 192392) ; or the catalyst may be a heavy metal oxide such as ferric oxide, with the addition of manganous oxide, zinc carbonate, magnesium oxide, etc. In B.P. 299048 the I.G. Farbenindustrie A.-G. claim the use of oxides, carbonates or acetates of alkaline earth metals, or of zinc, tin, aluminium, magnesium, etc., at 450°. In an example given by the Holzverkohlungs Industrie A.-G. (B.P. 280184), acetylene and steam when passed over rusty iron shavings at 500° are stated to afford quantitative yields of acetone. In later patents (B.P. 344449, 347695) Holzverkohlungs Industrie A.-G. pass acetylene and steam through a catalyst consisting of 10 cm. thick rolls of superficially treated iron gauze impregnated with suitable promoters, or alternatively a mixture of ethyl alcohol vapour, steam and acetylene is passed over rusty iron sponge containing 3% of manganese oxide at 470°, the yield of acetone being 89%. In U.S.P. 1779676, Martin, Krchma, and Commercial Solvents, Ltd., use as a catalyst mixtures of metal oxides and a metallic halide, *e.g.* the oxides of zinc, chromium, iron or nickel with zinc chloride. I.G. Farbenindustrie A.-G. prepare acetone from acetylene and steam by passage, at 350°–500°, over a catalyst consisting of various oxides such as those of sodium, potassium, magnesium, manganese, zinc, tin, chromium, aluminium, etc. (B.P. 330350). Similar claims form the subject of B.P. 353467 and 355362 (Groombridge, Oxley, Thomas, and British Celanese, Ltd.), according to which a mixture of alkaline-earth oxides or magnesium oxide is heated with zinc oxide to form a type of hydraulic cement, the product is ground up, hydrated, dried and used at 300°–500°C. to convert acetylene and steam directly into acetone. A suitable catalyst is made by depositing oxides or carbonates of calcium, magnesium, or chromium on iron sponge (Holzverkohlungs Industrie, A.-G., B.P. 315818) and an adjustable regenerative system of heating may be used (B.P. 339144) and, if desired, under pressure (B.P. 339148). The use of a cerium and cobalt catalyst is claimed in B.P. 316945 (Compagnie Générale des produits de Synthèse).

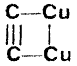
Pohl and the Deuts. Gold-und-Silber-Scheideanstalt vorm. Roessler pass acetylene and steam over various mixed catalysts (composed of the oxides of iron, manganese, cobalt, thorium, cerium, or tin with oxygenated compounds of magnesium, calcium, zinc, or aluminium) at 400°–500° and 13–15 atm. (U.S.P. 1953499 ; *cf. also* U.S.P. 1892742).

Platonov, Plakidina and Beltistov have examined a number of mixed catalysts for the conversion of acetylene to acetone, using zinc oxide+vanadium oxide, or ferric oxide at 425°–470°, the yields of acetone varying from 40–60% (J. Gen. Chem. Russ. 1934, **4**, 421). Uschakov and Rozengart obtained 90% conversion using a mixture of ZnO and MnO (4 : 1) as catalyst at 436°–440°. Zelinski (*ibid.* 1933, **10**, 63) has also investigated the problem. Zelinski, Uschakov, Mihkailov and Arbuzov claim a 98% conversion of acetylene to acetone by passing dilute acetylene and steam over a mixture of ferric oxide and manganese dioxide (7 : 3) as catalyst at 400° (J. Appl. Chem. Russ. 1934, **7**, 83).

(ε) **Metallic Derivatives.**—A characteristic property of acetylene and its congeners is their pronounced ability to form additive compounds and substitution products with metals and metallic salts. On heating with sodium a mixture of *sodium acetylide*, C_2HNa, and *sodium carbide*, C_2Na_2, is formed. Similar compounds are also known of lithium, potassium, cæsium and rubidium. With alkyl iodides, sodium acetylide reacts to form *homologues* of the acetylene series (*v.* Acetylenes ; *also* Lespieau and Journaud, Bull. Soc. chim. 1931 [iv], **49**, 423).

The compounds of acetylene with silver and copper are of particular interest ; these are formed on passing the gas through ammoniacal solutions of cuprous or silver salts ; the former is a brick-red precipitate of varying composition and is used as a test for the presence of the gas (*see* p. 96). It appears to have the composition $Cu_2C_2H_2O$ (or $Cu_2{\cdot}CH{\cdot}CHO$) (Makowka, Ber. 1908, **41**, 824). On heating gently it loses water yielding Cu_2C_2 ; Scheiber suggests the formulæ :

$CH{:}C{\cdot}Cu{\cdot}Cu(OH)$ and



(Ber. 1908, **41**, 3816 ; 1911, **44**, 210).

The silver compound has the formula C_2Ag_2,H_2O or $C_2H_2{\cdot}Ag_2O$, and forms a yellowish precipitate. Both the copper and silver compounds explode violently on heating or friction and some serious accidents have occurred owing to the accidental formation of copper acetylide in technical plant.

Acetylene also forms double compounds with salts of copper and silver, some of which are explosive, *e.g.* : $C_2H_2{\cdot}Cu_2Cl_2$; $C_2H_2{\cdot}2Cu_2Cl_2$; $C_2H_2{\cdot}3Cu_2Cl_2$, $CuSO_4{\cdot}2Cu_2C_2$; etc. The use of acetylene has been suggested as an analytical reagent for the separation of metals such as silver, copper, palladium, osmium, gold and mercury (Söderbaum, Ber. 1897, **30**, 760, 814, 902, 3014 ; Erdmann and Makowka, Z. anal. Chem. 1907, **46**, 128, 145 ; Scheiber, Ber. 1908, **41**, 3816 ; Scheiber and Reckleben, Ber. 1911, **44**, 210 ; Lavilla Llorens, Anal. Fís. Quím. 1912, **10**, 139 ; 1913, **11**, 320 ; Weaver, J. Amer. Chem. Soc. 1906, **36**, 2462).

With aluminium chloride in presence of alcohols, double compounds are formed, such as $AlCl_3{\cdot}2C_2H_2{\cdot}2H_2O$; $AlCl_3{\cdot}C_2H_2{\cdot}2EtOH$; $AlCl_3{\cdot}C_2H_2{\cdot}MeOH{\cdot}H_2O$ (Gangloff and Henderson, J. Amer. Chem. Soc. 1916, **38**, 1382 ; 1917, **39**, 1420 ; Baud, Compt. rend. **1900**, **130**, 1319 ; *cf. also* Hunter and Yohe, J. Amer. Chem. Soc. 1933, **55**, 1248). With acetylene and diethyl ether, aluminium chloride forms the liquid product : $2AlCl_3{\cdot}Et_2O{\cdot}C_2H_2$ (Hunter and Yohe, *l.c.*).

With magnesium bromide, compounds are formed such as $CH{:}CMgBr,({:}CMgBr)_2$ (Oddo, Atti R. Accad. Lincei, **1904** [v], **13**, 187 ; Gazzetta, 1908, **38**, i, 625 ; Yocichi, J. Russ. Phys. Chem. Soc. 1906, **38**, 1040). With magnesium ethyl bromide, acetylene reacts to form $BrMgC{:}CMgBr$ and ethane and on further treatment with acetylene under pressure $CH{:}CMgBr$ is produced, which reacts with carbon dioxide to form propiolic acid (Cheou, Contr. Inst. Chem. Nat. Acad. Peiping, 1934, **1**, 127 ; A. 1935, 1357). For the action of acetylene upon metallic magnesium, *see* Novák (Ber. 1909, **42**, 4209) and Cottrell (J. Physical Chem. 1914, **18**, 85).

The compounds of acetylene with mercury and with mercuric salts have been studied in some detail, as they are of considerable importance in view of the use of mercury salts as catalysts for the conversion of acetylene into acetaldehyde. *Mercuric acetylide* (or *carbide*), C_2Hg, is obtainable as a white, very explosive precipitate on passing the gas through Nessler solution (Keiser, Amer. Chem. J. 1893, **15**, 535) ; on treatment with acids acetylene is evolved. A hydrate, $3C_2Hg{\cdot}H_2O$, is also known (Plimpton and Travers, Trans. Chem. Soc. 1894. **65**, 226). On passing acetylene through an aqueous suspension of mercurous acetate in the dark, a hydrate of mercuro-acetylide is formed, $C_2Hg_2\,H_2O$ (Burkard and Travers, Trans. Chem. Soc. 1902, **81**, 1270). Mercuric acetate solution yields a slimy white precipitate of $3C_2Hg{\cdot}2HgO{\cdot}2H_2O$ (possibly $3C_2Hg{\cdot}2Hg(OH)_2$), which is not explosive and yields acetaldehyde but no acetylene, on treatment with acids (Burkard and Travers, *l.c.* ; Plimpton, Proc. Chem. Soc. 1892, **8**, 109). With a saturated acetic acid solution of mercuric acetate acetylene yields the explosive compound $2HgC_2{\cdot}C_2H_2{\cdot}H_2O$ (Färber and Römer, J. pr. Chem. 1934 [*ii*], **139**, 277). The compounds formed by the action of acetylene on mercuric chloride solutions are discussed in the article Acetaldehyde (p. 16).

When passed into alcohol in presence of a small amount of a mercury catalyst, acetylene yields *acetal* (*see* Acetals) ; with glacial acetic acid, *ethylidene diacetate* is formed, which can be readily split up into aldehyde and acetic anhydride (*see* Acetals). (*See also* Hofmann and Kirmreuther, Ber. 1908. **41**, 314 ; 1909, **42**, 4232.)

Spahr, Vogt, and Nieuwland (J. Amer. Chem. Soc. 1933, **55**, 2465, 3728) have shown that on passing acetylene into a solution of an appropriate organo-mercuri-halide in 10% aqueous potassium hydroxide, 80–90% yields are obtained of *di(organo-mercuri)-acetylides*, $[R{\cdot}HgC{:}]_2$ (*e.g.* $R{=}CH_3$, m.p. 323°–333°, decomp.; $R{=}C_2H_5$, m.p. 195°–196°). Their use is suggested for identification purposes.

(*f*) **Halogen Derivatives.**—(i) *Chlorine Derivatives.*—These form an important branch of the technology of acetylene and are therefore dealt with in a separate article (*see* Acetylene, Chlorine Derivatives of, p. 96).

(ii) *Bromine Derivatives.*— *Bromoacetylene*, $CBr{:}CH$, is formed by the decomposition of dibromoethylene with alcoholic potash :

$$CHBr : CHBr - HBr = CBr : CH.$$

It condenses to a colourless liquid, b.p. about −2°C. Both liquid and vapour are spontaneously inflammable. It burns vigorously in air, forming HBr, CO, $\mathrm{CO_2}$, and free carbon. Its solutions show phosphorescence and smell strongly like phosphorus. It polymerises in daylight, about 10% of the product being *sym*-tribromobenzene (Reboul, Annalen, 1863, **125**, 81 ; Schmeltz and Beilstein, Annalen, 1865, Spl. **3**, 280 ; Sabanejew, Ber. 1885, **18**, 374 ; Nef, Annalen, 1897, **298**, 355 ; 1899, **308**, 325 ; Gray, Trans. Chem. Soc. 1897, **71**, 1029).

Dibromoacetylene, $\mathrm{CBr}\vdots\mathrm{CBr}$, is formed by treating tribromoethylene with alcoholic potash (Lemoult, Compt. rend. 1903, **136**, 55 ; 1903, **137**, 1333 ; Lawrie, Amer. Chem. J. 1906, **36**, 490). It may also be formed by treating acetylene itself with hypobromites (I.G. Farbenind. A.-G., B.P. 333946).

Tetrabromoethane (*acetylene tetrabromide*), $\mathrm{C_2H_2Br_4}$, is formed readily by treating acetylene with excess of bromine (*cf.* Kali-Forschungs-Anstalt G.m.b.H., B.P. 381070). It is also formed by treating tetrachlorethane with aluminium bromide (Pouret, Bull. Soc. chim. 1901 [iii], **25**, 297), b.p. 114°/12 mm. Owing to its high density, d^{18} 2·971, it may be used for the analytical separation of minerals. An unsymmetrical tetrabromoethane is also known (Lennox, Annalen, 1862, **122**, 124 ; Sabanejew, Annalen, 1883, **216**, 255 ; Anschütz, Annalen, 1883, **221**, 140).

By removal of a molecule of HBr by means of dilute alkali, tho tetrabromo compound yields *tribromoethylene*, $\mathrm{CHBr : CBr_2}$, b.p. 163°–164°, d^{20} 2·708 (*cf.* Imbert and Consort. f. Elektrochem. Ind. G.m.b.H., G.P. 180011).

Treatment of tribromoethylene with alcoholic potash yields *dibromoacetylene*, $\mathrm{CBr}\vdots\mathrm{CBr}$, an unpleasant-smelling oil, b.p. 76°–77° ; it is very poisonous and spontaneously inflammable (Lemoult, Compt. rend. 1903, **136**, 55 ; 1903, **137**, 1333 ; Lawrie, Amer. Chem. J. 1906, **36**, 490) ; it adds on bromine to form *perbromoethylene* (tetrabromoethylene) (*v. infra*).

By the action of zinc and alcohol, or of amalgamated zinc on acetylene tetrabromide, *dibromoethylene* (*acetylene dibromide*) is produced. It is also formed by direct addition of dilute bromine solutions to acetylene in excess (*cf.* B.P. 381070). Direct addition of halogen yields a product having b.p. 110°, d^{17}=2·271. The product obtained by reduction of tribromoethylene consists of a mixture of the *cis* and *trans* isomers. One form has m.p. −6·5° and the other −53°; the mixture obtained consists of about one-third of the former and two-thirds of the latter (*cf. van de* Walle, Bull. Soc. chim. Belg. 1913, **27**, 209).

Perbromoethylene, $\mathrm{C_2Br_4}$, obtained by direct addition of bromine to dibromoacetylene (*v. supra*) or by the action of bromine upon an aqueous suspension of silver acetylide, or by distilling hexabromoethane, it forms colourless crystals, m.p. 56°, b.p. 226–227°C. With sodium ethoxide it yields *asym*-dibromovinyl ether, bromoacetic ester, tribromovinyl ether, and aldehyde resin (Nef, Annalen, 1897, **298**, **334**). Fuming nitric acid oxidises it to tribromoacetic acid or, in presence of conc. sulphuric acid, tribromoacetyl bromide is formed (Biltz, Ber. **1902**, **35**, 1536).

(iii) *Iodine Derivatives.*—Acetylene unites slowly with iodine to form *acetylene diodide* (sym. *diodoethylene*), $\mathrm{C_2H_2I_2}$, which exists in two stereo-isomeric forms, (1) m.p. 73°, b.p. 192° ; (2) m.p. −21°, b.p. 185°, d^{20} 3·06. With alcoholic potash the liquid form (2) yields acetylene and *di-iodoacetylene*, $\mathrm{C_2I_2}$. The solid form (1) can be converted into fumaric acid and is therefore the *trans* form, (2) yielding maleic acid and being therefore the *cis* form.

Di-iodoacetylene, $\mathrm{C_2I_2}$, is formed on treating calcium carbide with iodine (in aqueous potassium iodide), some tetraiodoethylene being also formed ; or by the action of an ethereal solution of iodine upon silver acetylide. It may also be prepared from tetraiodoethylene, or from iodopropiolic acid. It forms a white amorphous precipitate crystallising from ligroin in needles, m.p. 82°. It is an evil-smelling substance with a strong action upon the mucous membrane, and has marked antiseptic properties.

Magnesium acetylene iodide forms a thick, oily liquid (Yocichi, J. Russ. Phys. Chem. Soc. 1906, **38**, 1040).

(*g*) **Miscellaneous Reactions.**—(i) With *water* at low temperatures and under pressure, acetylene forms a hydrate, $\mathrm{C_2H_2,6H_2O}$. It does not, however, combine directly with water except in the presence of suitable catalysts. Thus by heating water with charcoal saturated with acetylene at 350° some acetaldehyde is formed (Desgrez, Ann. Chim. Phys. 1894 [vii], **3**, 216). Aldehyde is formed readily in presence of salts of cadmium, magnesium, zinc, or, best of all, mercury (Kutscherow, Ber. 1881, **14**, 1540 ; 1884, **17**, 13 ; 1909, **42**, 2759 ; Erdmann and Köthner, Z. anorg. Chem. 1898, **18**, 48), probably with intermediate formation of vinyl alcohol :

$$\mathrm{CH}\vdots\mathrm{CH}+\mathrm{HOH}\rightarrow\mathrm{CH_2:CH{\cdot}OH}\rightarrow\mathrm{CH_3{\cdot}CHO}$$

This property has in recent years given rise to many important developments as a successful industrial process, since acetaldehyde can be readily converted into various substances, such as ethyl alcohol, acetic acid, acetone, butadiene, butyl alcohol, etc. (*see* ALDEHYDE).

A saturated aqueous solution of acetylene after irradiation with light deposits a white inert polymer of acetylene (Livingston and Schiflett, J. Physical Chem. 1932, **36**, 750).

(ii) With *alcohols* in presence of a mercury catalyst, acetals are formed, *e.g.* :

$$\mathrm{CH}\vdots\mathrm{CH}+2\mathrm{EtOH}\rightarrow\mathrm{CH_3{\cdot}CH(OEt)_2}$$

(*see* ACETALS).

(iii) With *alkalis* at 220° hydrogen is liberated, with formation of alkali acetates (Feuchter, Ber. 1900, **33**, 2015 ; Chem.-Ztg. 1914, **38**, 273). A 60% yield is claimed, but it is doubtful if the process is of commercial value in view of the established method of synthesis of acetic acid from acetaldehyde (*cf. also* Dow Chemical Co., B.P. 363948).

(iv) With *fuming sulphuric acid* acetylene gives a sulphonic acid, the potassium salt of which, $\mathrm{C_2H_4O_2(SO_3K)_2}$, yields phenol on fusion with potash (Berthelot, Compt. rend. **1898**, 127, 908 ; 1899, **128**, 333 ; Ann. Chim. Phys. 1899 [vii], **17**, 289 ; Schroeter, Ber. 1898, **31**, 2189 ; Muthmann, *ibid.* 1880). With 50% fuming sulphuric acid the main product is *acetaldehyde disulphonic acid* :

$$CH{:}CH+2H_2SO_4 = (SO_3H)_2{\cdot}CH{\cdot}CHO+H_2O$$

(Schroeter, Muthmann, *l.c.*). Atterbury in B.P. 1208 (1898) claims the production of vinyl alcohol by passing acetylene into hot concentrated sulphuric acid.

(v) With *nitric acid*, nitroform and various complex nitrogenated substances are produced, including an explosive substance, $C_4H_2O_3N_4$, m.p. 78° (Testoni and Mascarelli, Gazzetta, 1901, **31**, 461 ; 1903, **33**, ii, 319). According to Quilico and Freri, however, fuming nitric acid produces an explosive compound, $C_4H_2O_7N_6$, which is reduced by stannous chloride to $C_4H_7O_3N_5$ (HCl salt, m.p. 182° decomp.), whilst with alkalis the orange-yellow substance $C_4H_5O_2N_5$ is formed. On heating the body $C_4H_2O_7N_6$ in glacial acetic acid nitrogen peroxide is evolved, leaving $C_4H_2O_3N_4$, which is probably an *iso*oxazole derivative (Gazzetta, 1930, **60**, 721 ; 1931, **61**, 265, 464, 759). According to Orton (B.P. 125000) a good yield of tetranitromethane may be obtained by passing acetylene into 90–97% nitric acid, preferably in presence of a small quantity of mercuric nitrate, at about 40°, adding sulphuric acid and distilling off the tetranitromethane so formed.

(vi) *Sulphur Derivatives.*—Although *thiophen* is not readily formed directly from acetylene and sulphur (*cf.* Capelle, Bull. Soc. chim. [iv], **3**, 154 ; de Coninck, Bull. Acad. roy. Belg. 1908, 303), it is obtainable in good yield by passing acetylene over heated pyrites at 280°–310° (Steinkopf and Kirchoff, Annalen, 1913, **403**, 1 ; G.P. 252375 ; B.P. 16810, 1912 ; F.P. 446136). Tschitschibabin, however, claims to obtain a purer product by the use of hydrogen sulphide than by Steinkopf's method (J. Russ. Phys. Chem. Soc. 1915, **47**, 702). Thiophen is also produced by passing acetylene mixed with hydrogen sulphide over nickel hydroxide mixed with cement, or over partially reduced bauxite (Chem. Fabr. Rhenania, B.P. 109983). In B.P. 316282 (I.G. Farbenind. A.-G.) a mixture of products of the pyridine and thiophen series is obtained by passing a mixture of acetylene and ammonium sulphide over heated metallic sulphides. Bhatt and others have investigated the action of acetylene upon molten sulphur at 290°–390°, obtaining carbon, hydrogen sulphide, thiophen and phenyl mercaptan (A. 1935, 325).

(vii) *Nitrogen Derivatives.*—A number of technical investigations have been directed towards the possibility of synthesising nitrogenous bases from acetylene by heating it with ammonia, etc. Thus a product consisting largely of *acetonitrile* is obtained by passing acetylene and ammonia over bauxite, brown iron-stone, etc., at 350° (Stuer, Grob, and Chem. Fabrik Rhenania, G.P. 365432, 415684). A similar process is also claimed by I.G. Farbenindustrie A.-G. (B.P. 283163, 295276) ; in this case by using the oxides of zinc, thorium, zirconium, etc., deposited upon alumina gel or silica gel, at 450°, the product consists of *acetonitrile* and *pyridine bases*, whilst by using zinc chloride, with or without ferric chloride, or cadmium chloride with cupric chloride, at 280°–350°, a product is obtained consisting of 15–20% *diethylamine*, 5–6% *triethylamine*, and other aliphatic bases, 60–65% of *a*- and *γ-methylpyridine*, and 10–12% of higher methylpyridines and polynuclear bases, whilst *quinaldine* is obtained by passing acetylene and aniline over heated pumice coated with zinc chloride, acetylene, and ethyl-aniline, affording a mixture of *quinaldine*, N-*ethylquinaldine*, and N-*ethyl indole* (I.G. Farbenindustrie A.-G., B.P. 296423). By passing acetylene into aniline containing cupric chloride, at 90°C., *antioxidants* for rubber are obtained (Imperial Chemical Industries, Ltd., B.P. 348985). The synthesis of *acetic ester* from acetylene and ammonia, *via* the nitrile and alcohol, is claimed in B.P. 366106 (I.G. Farbenind. A.-G.) ; *acetonitrile* and other nitrogenous substances are obtained by passing a mixture of acetylene and ammonia over silica gel containing zinc sulphate (B.P. 332258), and the product is hydrolysed continuously to acetic acid by means of hot, fairly strong sulphuric acid (B.P. 339235). *Picoline, lutidine* and *collidine* are the main products obtained on passing acetylene and ammonia, below 350°, over lead, cadmium, bismuth or gold on a porous carrier (B.P. 321177) ; or the same mixture may be passed over silica gel containing a compound of zinc, aluminium, cadmium, etc., at 350° or over, to produce a mixture of heterocyclic bases (B.P. 332623) ; or acetylene with ammonia, steam and hydrogen may be passed over suitable catalysts to yield a mixture of aliphatic and reduced heterocyclic bases, *e.g.* *ethylamine*, *piperidine*, etc. (B.P. 334193).

On treating acetylene with hydrocyanic acid (*e.g.* by treating powdered calcium carbide and potassium cyanide with dilute sulphuric acid, and evaporating the residue) a 5% yield of succinic acid is obtained, pointing to the intermediate formation of *succinonitrile* (Commanducci, Chem.-Ztg. 1911, **35**, 383).

(viii) *General Reactions.*—A 70% yield of *propylene* is claimed by Heinemann by passing a mixture of acetylene and methane over heated contact substances (B.P. 12365, 1913 ; U.S.P. 1134677) :

$$CH{:}CH+CH_4 \rightarrow CH_3{\cdot}CH:CH_2$$

The catalyst recommended is platinum and copper, or aluminium and magnesium on pumice at 100°–200°.

By allowing acetone or its homologues to act upon the alkali compounds of acetylene (*e.g.* by passing acetylene into acetone in presence of sodamide), *γ-methyl-Δ^a-butinen-γ-ol* or its homologues are produced :

$$(CH_3)_2CO+CH{:}CNa \rightarrow (CH_3)_2C(OH)C{:}CH$$

(Farbenf. vorm. Fr. Bayer, G.P. 285770). The same result may be obtained by allowing acetone and acetylene to interact in the presence of alkali alkoxides (G.P. 284764, 286920, 289800). On reduction, the product yields *γ-methyl-Δ^{α}-butylen-γ-ol* (G.P. 288271),

$$(CH_3)_2C(OH)CH : CH_2$$

which can then be dehydrated to *β-methylbutadiene* (*isoprene*) and polymerised to synthetic rubber.

Hess and Munderloh (Ber. 1918, **51**, 377) obtained negative results on attempting to condense sodium acetylide with ketones or aldehydes, but on mixing sodium acetylide with dry sand, and treating with carbon dioxide under pressure for fourteen days, *sodium propiolate*, $CH : C{\cdot}COONa$, was obtained. The free acid distilled at 55°–56°/25 mm., and solidified on cooling (Strauss and Voss, G.P. 411107).

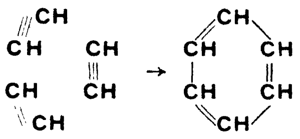
(ix) *Phenol-acetylene Condensation Products.*—*Resinous products* soluble in alcohol and benzene may be obtained by passing acetylene into a mixture of cresols and sulphuric acid, containing mercuric sulphate and ferric chloride (Melamid, B.P. 103679). Similar claims are contained in B.P. 183830 (Nieuwland and Shawinigan Labs., Ltd.). The process is slightly modified by Canadian Electro Products, Ltd., in that the condensation product of acetylene and a phenol is subsequently condensed with acetaldehyde in presence of sulphuric acid and mercuric sulphate (B.P. 232277). Resinous products of the cuprene or aldehyde types are produced by the interaction of acetylene with a large variety of organic substances (B.P. 228157, Consort. f. Elektrochem. Ind. G.m.b.H.).

(x) *Diolefines* may be obtained by heating molecular proportions of an ethylene hydrocarbon and an acetylene hydrocarbon, under pressure, in presence of a catalyst such as an oxychloride, molybdic acid, or an oxide or hydroxide of an alkali or alkaline earth ; thus acetylene and ethylene yield $\Delta^{\alpha\gamma}$-butadiene ; a hydrocarbon (isoprene ?) is formed from acetylene and propylene, and by gradually increasing the temperature and pressure the diolefine produced can be polymerised (Traun's Forschungslaboratorium, B.P. 156116, 156119).

Acetylenic alcohols, $CR : C{\cdot}CH_2{\cdot}OH$, are readily obtained by the action of gaseous formaldehyde on the magnesium bromide derivative of the corresponding acetylene ; alcohols such as phenylpropiolic alcohol have fragrant odours (Guest, J. Amer. Chem. Soc. 1925, **47**, 860).

V. POLYMERISATION REACTIONS.

(*a*) **Pyrogenetic Condensations.**—On heating acetylene it undergoes various condensations which are of great technical importance in connection with the theory of gas manufacture and, more recently, in connection with the hydrogenation of coal and lignite and the production of "synthetic petrol." The classical investigations of Berthelot (Ann. Chim. Phys. 1868 [iv], **9**, 446, 469 ; Jahresber. f. Chem. 1866, 516) showed that on leaving acetylene for a time in a glass tube heated to its softening point, a mixture of solid and liquid hydrocarbons was formed in which benzene predominated :



It therefore appears probable that the formation and thermal polymerisation of acetylene play an important part in the production of aromatic hydrocarbons in the manufacture of coal-gas (*cf. also* Haber, Ber. 1896, **29**, 2691 ; Lewis, Proc. Roy. Soc. 1894, **55**, 90; 1895, **57**, 394). R. Meyer and his co-workers have found that on passing acetylene through a tube suitably heated in an electric furnace large quantities of tarry products are produced, over 20% being benzene, and they were able to isolate and identify some 23 products, identical with those occurring in ordinary gas-tar (R. Meyer and others, Ber. 1912, **45**, 1609 ; 1913, **46**, 3183 ; 1914, **47**, 2765 ; 1917, **50**, 422 ; 1918, **51**, 1571).

Bone and Coward, however, take a different view, holding that the main gaseous product at high temperatures must be methane, which may dissociate into free radicals, CH : and CH_2 : and these combine together in various ways as the gases cool down (J.C.S. 1908, **93**, 1197). This point of view requires consideration in the light of more recent work upon the synthesis of acetylene by pyrolysis of methane at very high temperatures.

Berl and Hofmann (Z. angew. Chem. 1931, **44**, 259) have found that in presence of carbon as a catalyst acetylene readily polymerises at 600°–800° to aromatic hydrocarbons, a nearly theoretical conversion being claimed at 760°. Metallic catalysts proved unsatisfactory. Fischer and Peters (Brennstoff-Chem. 1931, **12**, 286) found that in contact with a nickel-thorium-aluminium-kieselguhr catalyst suspended in a high-boiling paraffin, a mixture of acetylene and hydrogen gave an 80% yield of liquid hydrocarbons at temperatures above 200°C. Binnie has shown that nickel carbonyl is a suitable catalyst for condensing dilute acetylene to a complex oil *d* 0·69, with a yield of 60% (J.S.C.I. 1931, **50**, 297T). Petrov and Antzus (J. Appl. Chem. Russ. 1933, **6**, 1145 ; A. 1934, 277) showed that on heating a 1 : 5 mixture of acetylene and hydrogen at 170°/18 atm. ethane was yielded quantitatively, whilst a 1 : 1 : 4 mixture of acetylene, hydrogen, and nitrogen gave 80% of naphthenic hydrocarbons. The polymerisation of acetylene in presence of hydrogen has also been studied by Pichler (Gesamm. Abh. Kenntn. Kohle, 1934, **11**, 395, 401; B. 1935, 394). Neumann, utilising a catalyst consisting of Fe 9·0+Ni 0·5+Cu 0·5, obtained a 60% yield of liquid hydrocarbons from acetylene (*ibid.* 423, 434 ; B. 1935, 394). Mignonac and Ditz (Compt. rend. 1934, **199**, 367) by polymerisation of acetylene at

750° in a silica tube obtained benzene and a yellowish-green polymer, b.p. 7°, C_4H_4 (*chlorene*), which appeared to pass into benzene on standing. Klatt (Erdöl und Teer, 1934, **10**, 241, 253, 265) obtained a good yield of condensation products by passing acetylene+20% steam over a graphitised or unglazed earthenware catalyst at 600°. Lozovoj (J. Gen. Chem. Russ. 1931, **1**, 717) obtained liquid products containing olefines, benzene, toluene and naphthalene by passing acetylene over pumice+5% zinc chloride, at 420°–430°.

For a complete discussion of the subject, *see* "The Pyrogenesis of Hydrocarbons," Part I, E. L. Lomax ; Part II, A. E. Dunstan and F. B. Thole, Ind. Eng. Chem. 1917, **9**, 879, 888 ; J. Inst. Petroleum Tech. 1916, **3**, 36. A comprehensive bibliography is given in the article. *See also* Hilpert, Gesamm. Abh. Kenntn. Kohle, 1917, **1**, 271 ; Egloff and Wilson, Ind. Eng. Chem. 1935, **27**, 917 ; and Taylor and van Hook, J. Physical Chem. 1935, **39**, 811.

The technical importance attached to the development of processes having for their object the production of liquid hydrocarbons such as *benzene*, etc., may be gauged from the following typical investigations and patented processes published in recent years : Zelinski (Ber. 1924, **57**, [B] 264) showed that when acetylene is passed through a tube packed with activated wood charcoal at 640°–650° about 70–80% is converted into a tar consisting chiefly of aromatic hydrocarbons, 35% of which consists of benzene, toluene, xylene, styrene, and indene. Crude acetylene from methane, etc., is converted into liquid hydrocarbons by passing the gaseous mixture over activated charcoal or silica gel at 600°–700°C. (Fischer, Bangert, and Pichler, Brennstoff-Chem. 1929, **10**, 279). Using undiluted acetylene the yield of products is higher, but in both cases the light-oil fraction, boiling up to 150°, forms 50% of the total oil. The formation of light oil is favoured by the addition of carbon dioxide to the gases, the carbon deposited during the condensation acting as a catalyst. Using an acetylene-hydrogen mixture in presence of catalysts at 250°, 40–70% of the acetylene is converted into oil (Fischer, Peters, and Koch, Brennstoff-Chem. 1929, **10**, 383). Closely connected with this subject is B.P. 128660 (F. M. Perkin and Nitrogen Products, Ltd.), which claims increased yields of benzene in a process of destructive distillation (given in B.P. 114937), by mixing 2·5–10 parts of acetylene with the gas which is passed through the retorts to assist in the carbonisation. In B.P. 211461 (F. Gros) acetylene is passed through tubes containing rings of electrode carbon heated by an electric current, and the liquid products separated by absorption or cooling. I.G. Farbenind. A.-G., in B.P. 265234 (void), subject gaseous hydrocarbons such as methane to incomplete combustion with pure oxygen at temperatures above 850°C. in a quartz or iron tube filled with porous material. Gessman and Shalders (B.P. 299820) obtain low-boiling hydrocarbons by passing a mixture of acetylene, hydrogen and carbon monoxide over a metallic catalyst such as copper and tungsten deposited upon pumice which is irradiated with ultra-violet light at intervals of two hours, without heating. Ylla-Conta (B.P. 299425, 301325) claims the production of benzene, etc., from acetylene by heating the gas in an iron or steel vessel to a suitable reaction temperature, and causing this gas to circulate through an external refrigerator, separating the condensed polymerisation products and recirculating the gaseous portion. I.G. Farbenindustrie A.-G. obtain hydrobenzenes by passing acetylene and hydrogen over zinc chloride deposited upon silica gel at 450° and then over nickel at 200°C. (B.P. 344443, 348604). Producer gas admixed with methane or acetylene affords a liquid fuel on treatment at 80°C. with a catalyst consisting of cerium and cobalt sulphates (Comp.-Gén. des Produits de Synthèse, B.P. 316945). The polymerisation of olefines and acetylene to oils by heating the gases in contact with elements of the 4th periodic group, such as tin, silicon, lead or graphite, or with zinc, aluminium, or various metallic chlorides, is claimed in B.P. 316422 by I.G. Farbenindustrie A.-G. An almost theoretical conversion of acetylene into benzene hydrocarbons by catalytic thermal treatment in which cooled surfaces are located immediately opposite the heated catalytic surfaces is claimed in B.P. 374422 (Ruhrchemie A.-G.). *See also* B.P. 334203 (I.G. Farbenind. A.-G.), B.P. 344470 (N. V. de Bataafsche Petroleum Maatsch.). Ruhrchemie A.-G. describe details of a process for the partial conversion of methane to acetylene, followed by pyrogenetic condensation to benzene hydrocarbons, in B.P. 373249, 373822, 374055, and 374422 ; for instance, methane is passed through a tube heated to 2,000°C. for a short time and then through a porcelain tube heated to 600°C. containing a central copper tube heated to 100°C. A conversion yield of 65% is claimed.

For references to work on the *photochemical polymerisation* of acetylene, *see* Lind and Livingston, J. Amer. Chem. Soc. 1930, **52**, 4613 ; 1932, **54**, 94 ; Kemula and Mrazek, Z. physikal. Chem. 1933, B, **23**, 358 ; Livingston and Schiflett, J. Physical Chem. 1934, **38**, 377 ; Lind and Livingston, J. Amer. Chem. Soc. 1934, **56**, 1550 ; Toul, Coll. Czech. Chem. Comm. 1934, **6**, 162 (A. 1934, 852) ; *cf. also* Kemula, *ibid.* 1935, **7**, 319 (A. 1935, 1208).

Prolonged heating above 800° or so causes the decomposition of acetylene into hydrogen and free carbon, possibly with intermediate formation of methane :

$$2C_2H_2=3C+CH_4=4C+2H_2$$

(*cf.* Bone and Coward, J.C.S. 1908, **93**, 1197). This method is of industrial importance, partly as a means for producing hydrogen but mainly for the manufacture of *acetylene black* (*cf.* J.S.C.I. **17**, 8, 711 ; **18**, 284 ; **20**, 890, 955 ; Frank, Z. angew. Chem. 1905, **18**, 1733 ; Dawson and Hartshorne, Trans. Inst. Rubber Ind. 1930, **5**, 48 ; Morehead, U.S.P. 986489 ; Pictet, B.P. 24256, 1910 ; Machtolf and Hostmann-Steinbergersche Farbenfabrik, U.S.P. 1178540). Prior to the war the Carbonium Co. had a factory at Friedrichshafen in which compressed acetylene was decomposed electrically to produce acetylene black and hydrogen ; it is doubtful whether this method for producing hydrogen can compete with other and cheaper methods such as the Messerschmidt or Frank-Caro processes (*vide* HYDROGEN).

Acetylene burns with a characteristic smoky but brilliantly white flame which can be modified by mixing carbon dioxide with the gas, the intensity varying with the concentration of the latter (*see also* ACETYLENE, ITS USE IN INDUSTRY).

When submitted to the action of an electric discharge at ordinary pressure, various condensation and polymerisation products are formed (*see* Berthelot, Bull. Soc. chim. 1890 [iii], **4**, 480 : Jackson and Laurie, Chem. Soc. Proc. 1906, 155 ; Losanitsch, Monatsh. 1908, **29**, 753 ; Jovitschitsch, *ibid.* **29**, 1, 5 ; Coehn, Z. Elektrochem. 1901, **7**, 681 ; Billitzer, Monatsh. 1902, **23**, 199 ; Schützenberger, Compt. rend. 1890, **110**, 889 ; Kaufmann, Annalen, 1919, **417**, 34 ; Lund and Schultze, Trans. Amer. Electrochem. Soc. 1931, **59**, 141 ; de Saint-Aunay, Chim. et Ind. 1933, **29**, 1011 ; Mund and Jungers, Bull. Soc. chim. Belg. 1931, **40**, 158).

(*b*) **Cuprene.**—A solid polymerisation product of acetylene termed *Cuprene* (or *Carbene*) is obtained from acetylene in various ways, *e.g.* heating in presence of copper, or by the action of a silent electric discharge (Elektrizitätswerk Lonza, B.P. 189146, 192080), the losses due to coking being reduced by the addition of 5–15% by volume of nitrogen to the acetylene (B.P. 200087). A form of cuprene suitable for decolorising liquids is obtained by passing acetylene at 200°–400° over a metal or metal oxide catalyst, such as copper, nickel, iron or their oxides, to which a small proportion of magnesium has been added (N. V. "Electro" Zuur-en Waterstof-fabr., B.P. 303797 ; *see* Ellis, "Chemistry of Synthetic Resins" (New York, 1935), Vol. II, p. 1077).

A hard, brittle variety of cuprene is obtained by passing acetylene with 10–15% of nitrogen over a catalyst consisting of $CuO+1\%SnO_2$ at 250°–260° (David and Levy, B.P. 418005). A product termed *Carbene*, used for the preparation of blasting cartridges, is prepared by adding iron powder to a carbon carrier, treating with copper sulphate and using this as a catalyst for effecting the condensation of acetylene. Foulon (Z. ges. Schiess-u.-Sprengstoffw. 1932, **27**, 48) summarises the patent literature upon cuprene, showing its application as a substitute for charcoal in blackpowder and other explosives, etc. Kaufmann and Schneider (Ber. 1922, **55**, 267 ; 1923, **56**, 2533) discuss the constitution of cuprene, whilst the chemistry and applications of cuprene are reviewed by Herzog in Chem.-Ztg. 1931, **55**, 461. Technically it is possible to obtain 1 kg. of crude cuprene from 4 kg. of calcium carbide, the product varying from a dark-coloured flocculent substance to granular cork-like lumps. The products obtained consist of about 75–80% cuprene, 13–17% of waste gases, and 5·5–7% of cuprene tar ; the nature of the tar is discussed by Schläpfer and Stadler (Helv. Chim. Acta, 1926, **9**, 185).

(*c*) **Vinyl Acetylene, Divinyl Acetylene, etc.**—An important new development in the technical utilisation of acetylene has arisen from the discovery of Nieuwland that it is readily polymerised by aqueous solutions of cuprous ammonium chloride to yield *vinylacetylene* and *divinylacetylene* :

$$2CH\vdots CH \rightarrow CH_2{:}CH{\cdot}C\vdots CH$$

Vinylacetylene.

$$(+CH\vdots CH) \rightarrow CH_2{:}CH{\cdot}C\vdots C{\cdot}CH{:}CH_2$$

Divinylacetylene.

Investigations of these compounds by Nieuwland and his students in co-operation with Carothers and the Du Pont de Nemours & Co. Research Dept. have led to valuable new products, in particular to the synthesis of β-chlorobutadiene ("Chloroprene") and from this the new synthetic rubber *Duprene* (*Duroprene*).

Vinylacetylene is a colourless liquid with a sharp, sweetish odour, b.p. 5·8°C., and was first prepared by Willstätter and Wirth (Ber. 1913, **46**, 538) by distilling the substance

$$HO{\cdot}NMe_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$$

under reduced pressure (*see also* Shilov, Makashina, Smirnova, and Yakimov, Sintet. Kauchuk, 1933, I, 4 ; A. 1934, 55). A general account of the reactions of acetylene with cuprous ammonium chloride solutions under various conditions is given by Carter, Downing, Calcott, and Nieuwland (J. Amer. Chem. Soc. 1931, **53**, 4197), and by Nieuwland (Ind. Eng. Chem. 1935, **27**, 852–853). Using a mixture of 3 parts by weight of cuprous chloride, 1 part water, and 1 part ammonium chloride, vinyl and divinylacetylenes are formed on passing in acetylene ; the chlorides of alkali metals or of alkaline earths may be used but are not so effective ; presumably ammonium cuproso chloride is formed. The mechanism of the polymerisation is still obscure. The copper compound of divinylacetylene is a lemon-yellow crystalline substance which partially dissolves in the catalytic mixture. In presence of concentrated hydrochloric acid, vinyl chloride and *cis-* and *trans-*dichloroethylene are also formed.

The main process is described in B.P. 384654 (Du Pont de Nemours & Co.) and consists in passing acetylene into an agitated mixture of ammonium chloride, cuprous chloride, copper powder and water at about 25°C., the acetylene polymers being distilled off after the absorption of gas has slackened ; the ammonium salt may be replaced by the salt of a tertiary amine and the solution preferably has a p_H of 6·0 or less, some undissolved salts being present to ensure saturation ; the original process is modified in B.P. 390179 (addn. to B.P. 384654) by including in the catalytic solution an acid of ionisation constant of at least 10^{-6}, *e.g.* a small quantity of hydrochloric, hydrobromic or hydriodic acid, sulphuric or phosphoric acid, or a carboxylic acid such as acetic, chloracetic, formic, tartaric, citric acids, etc. In examples there are used :

	Parts		Parts.
CuCl . . .	70		17·8
$\mathrm{NH_4Cl}$ . .	27		—
Cu powder . .	7	or	3·0
$\mathrm{H_2O}$ . . .	30		—
HCl (37%) . .	2·1		—
$\mathrm{CH_3{\cdot}COOH}$.	—		38·3
Pyridine . .	—		42·7

In B.P. 401678 (addn. to B.P. 384654) the production of vinylacetylene is claimed by continually removing it from the reaction mixture before substantial amounts of divinylacetylene have been formed, for example, by constant circulation of an excess of acetylene and separation of the reaction products. The time of contact is about 10–15 secs. ; the reaction products may also be removed in a countercurrent of mineral oil, etc. (*see also* Nieuwland, Vogt, Downing, Carter, Hutton, and Du Pont de Nemours, U.S.P. 1926055, 1926056, 1926039).

Perkins, Toussaint, and the Carbide and Carbon Chemical Corp. prepare a suitable catalyst by heating a solution of CuCl (300 pts.), $\mathrm{NH_4Cl}$ (300 pts.) in water (600 pts.) and conc. HCl (70 pts.) to 90°C., filtering, passing in acetylene until any cupric salt is reduced to the cuprous condition, adding ammonia until a permanent black deposit is formed and redissolving in the minimum amount of hydrochloric acid ; the acetylene is then passed in at 70°C., the resultant vinylacetylene being continuously removed either by excess acetylene or by a non-miscible solvent (U.S.P. 1971656).

Klebanski, Zurich, Dolgopolski, *et alia* state that a 75–80% yield of vinylacetylene is obtainable together with 20–30% of trimerides and higher polymers, about 40% of acetylene being converted in a single passage through the catalyst (Bull. Acad. Sci. U.R.S.S. 1935, **2**, 189–226 ; Klebanski, Dranitzina, and Dobromilskaja, *ibid.* 1935, **2**, 229).

In addition to vinyl- and divinylacetylenes there are also formed smaller amounts of *acetylene-divinyl*, $\mathrm{CH_2 : CH{\cdot}CH : CH{\cdot}C \vdots CH}$, b.p. 30°–32°/100 mm., and a tetramer, $\mathrm{C_8H_8}$, b.p. 40°–44°/20 mm., possibly *αεη-octatrien-γ-inc* (Carter, Downing, Calcott, and Nieuwland, *l.c.* ; Klebanski, etc., *l.c.*).

Gelatinous or resinous polymerisation products may be obtained by heating vinylacetylene in absence of air to 50°–110°, with or without a catalyst (Du Pont de Nemours, B.P. 385963, 389109 ; Dykstra, J. Amer. Chem. Soc. 1934, **56**, 1625). With methyl alcohol in presence of an acid mercury catalyst, vinyl acetylene forms the substance

$$\mathrm{(OMe)_2CMe{\cdot}CH_2{\cdot}CH_2{\cdot}OMe}$$

(Killian, Hennion, and Nieuwland, J. Amer. Chem. Soc. 1934, **56**, 1786), whilst with acetic acid in presence of mercury salts and methoxyfluoboric acid, 2-*acetoxybutadiene* (*butadien-β-yl acetate*) is formed (the acetoxy isologue of isoprene) :

$$\mathrm{CH_2{=}C(OAc){\cdot}CH{=}CH_2},$$

b.p. 52°–54°/40 mm., which polymerises spontaneously to a beautiful transparent flexible rubber-like substance, and with hot 5% sulphuric acid yields methyl vinyl ketone,

$$\mathrm{CH_2 : CH{\cdot}COMe},$$

(Nieuwland, Ind. Eng. Chem. 1935, **27**, 853 ; Werntz, J. Amer. Chem. Soc. 1935, **57**, 204).

With mercury salts, *e.g.* $\mathrm{K_2HgI_4}$, vinylacetylene forms mercury divinylacetylide,

$$\mathrm{[CH_2 : CH{\cdot}C{\equiv}C]_2 : Hg}$$

(Carothers, Berchet, and Jacobson, J. Amer. Chem. Soc. 1933, **55**, 4665). The partial hydrogenation of vinyl acetylene is referred to in B.P. 389108 (Du Pont de Nemours). With a solution of mercuric acetate at 60°–70° vinylacetylene yields the compound

$$\mathrm{CH_2 : CH{\cdot}C(O{\cdot}Hg{\cdot}OAc) : C(Hg{\cdot}OAc)_2}$$

(Carothers, Jacobson and Berchet. J. Amer. Chem. Soc. 1933, **55**, 4665), whilst in 30 to 50% sulphuric acid in presence of mercury, copper, sliver, cadmium or zinc salts, vinylacetylene is hydrated to *methyl vinyl ketone*,

$$\mathrm{CH_2 : CH{\cdot}CO{\cdot}CH_3}$$

(Carter, Downing, and Du Pont de Nemours, U.S.P. 1896161–2 ; Conaway and Du Pont de Nemours, U.S.P. 1967225 ; B.P. 388402). With ethyl magnesium bromide, vinylacetylene forms vinyl-ethinyl magnesium bromide,

$$\mathrm{CH_2 : CH{\cdot}C \vdots C{\cdot}MgBr},$$

which reacts normally, *e.g.* with acetone to yield vinyl-ethinyl-dimethyl carbinol :

$$\mathrm{CH_2 : CH{\cdot}C \vdots C{\cdot}CMe_2{\cdot}OH},$$

b.p. 67°/24 mm., 140°–142°/760 mm., which polymerises on standing to a colourless transparent resin (Carothers and Berchet, J. Amer. Chem. Soc. 1933, **55**, 1094). Sodium or sodamide reacts with vinylacetylene to yield *sodium vinylacetylide*, a white powder which reacts with acetaldehyde to yield

$$\mathrm{CH_3{\cdot}CH(OH){\cdot}C \vdots C{\cdot}CH : CH_2},$$

b.p. 65°/22 mm., and with acetone to give vinylethinyl dimethyl carbinol (*v.s.*) (Carothers and Jacobson, J. Amer. Chem. Soc. 1933, **55**, 1097 ; Carothers, Berchet, Jacobson, and Du Pont de Nemours, Ltd., U.S.P. 1963934, 1963935, 1963074). With alkyl halides sodium vinylacetylide reacts to form α-alkyl-β-vinylacetylenes, *e.g.* α-ethyl-β-vinylacetylene,

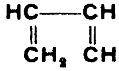
$$\mathrm{C_2H_5{\cdot}C \vdots C{\cdot}CH : CH_2},$$

b.p. 84°–85° (Carothers and Jacobson, J. Amer. Chem. Soc. 1933, **55**, 1622). In presence of sodium alkoxides at 100°, vinylacetylene adds on alcohols to yield unsaturated ethers of the type $\mathrm{CH_3{\cdot}C \vdots C{\cdot}CH_2{\cdot}OR}$ (Jacobson, Dykstra, and Carothers, J. Amer. Chem. Soc. 1934, **56**, 1169). Successive treatment of vinylacetylene, in liquid ammonia, with sodamide and dimethyl sulphate affords α-methyl-β-vinylacetylene, b.p. 59° ; α-ethyl-β-vinylacetylene, b.p. 84·5°–85·5° is formed in a similar manner (Jacobson and Carothers, J. Amer. Chem. Soc. 1933, **55**, 1622).

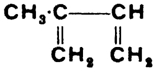
A general summary of the additive reactions of acetylene, vinylacetylene and divinylacetylene may be found in the Annual Reports on the Progress of Chemistry of the Chemical Society, 1933, 133–6 ; 1934, 162–3 ; *see also* Ellis, "Chemistry of Synthetic Resins," Vol. I, p. 149 (New York, 1935).

Halogen Derivatives of Vinylacetylene.—With aqueous hypohalides (*e.g.* $NaOCl$) vinylacetylene reacts to form the corresponding α-substituted derivative, of which the *α-chloro-* has b.p. 55°–57°/760 mm., the *α-bromo* b.p. 52°–53°/287 mm., and the *α-iodo* b.p. 78°/125 mm. The halogen compounds are explosive and readily polymerise to explosive black substances (Carothers and Jacobson, J. Amer. Chem. Soc. 1933, **55**, 4667).

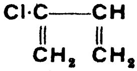
In contact with a solution of cuprous chloride and ammonium chloride vinylacetylene adds on one molecule of hydrochloric acid to form δ-chloro-$\Delta^{\alpha\beta}$-butadiene, b.p. 88°, which isomerises at once to form *β-chloro-*$\Delta^{\alpha\gamma}$*-butadiene* (2-*chloro-butadiene* 1 : 3), $CH_2:CCl{\cdot}CH:CH_2$, a colourless liquid, b.p. 59·4°/760 mm.—6·4°/100 mm. This substance, to which the name *chloroprene* has been given, is the chlorine analogue of isoprene (2-methyl-butadiene 1 : 3). The formyl analogue is called *formoprene* (*v.infra*).


$\begin{array}{ll} HC & \!\!-\!\!-CH \\ \| & \;\;\| \\ CH_2 & CH_2 \end{array}$

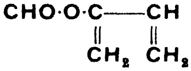
Butadiene.


$\begin{array}{ll} CH_3{\cdot}C & \!\!-\!\!-CH \\ \quad\;\| & \;\;\| \\ \quad CH_2 & CH_2 \end{array}$

Isoprene.


$\begin{array}{ll} Cl{\cdot}C & \!\!-\!\!-CH \\ \| & \;\;\| \\ CH_2 & CH_2 \end{array}$

Chloroprene.


$\begin{array}{ll} CHO{\cdot}O{\cdot}C & \!\!-\!\!-CH \\ \qquad\quad\| & \;\;\| \\ \qquad\quad CH_2 & CH_2 \end{array}$

Formoprene.

Chloroprene polymerises readily in a closed vessel to form a plastic polymeride, μ-polychloroprene, which closely resembles a completely vulcanised rubber ; by interrupting the polymerisation a less highly polymerised product, α-polychloroprene, is obtained, resembling unvulcanised rubber, which changes into the μ-variety at 30° (Carothers, Berchet, and Collins, J. Amer. Chem. Soc. 1932, **54**, 4066 ; Carothers, Collins, Kirby, and Williams, *ibid.* 1931, **53**, 4203 ; 1932, **54**, 4066 ; B.P. 387325, Du Pont de Nemours & Co.). With metallic sodium, chloroprene forms an ω-polymeride as hard rubbery granules.

According to Zelinski, Kozlov, and Schter (Bull. Acad. Sci. U.R.S.S. 1934, **8**, 141), chloroprene is formed in 80% yield by shaking vinylacetylene with conc. hydrochloric acid at room temperature in presence of cuprous and ammonium chlorides. The process may be carried out continuously by circulating vinylacetylene through a suitable system containing the necessary catalyst (B.P. 395131, Du Pont de Nemours & Co.). Chloroprene condenses with maleic anhydride to form 4-chloro-1 : 2 : 3 : 6-tetrahydrophthalic acid (*see also* Ellis, "Chemistry of Synthetic Resins," Vol. I, p. 154, New York, 1935).

The ι-polychloroprene is now made commercially by Du Pont de Nemours & Co., under the name of "*Duprene*," and in spite of its relatively high price is finding wide applications on account of its great resistance to water, oxygen, acids, petrol and oils, in which respects it is superior to natural rubber. It is understood also that its manufacture in Russia is being developed. Chloroprene may be dispersed in a suitable medium such as aqueous sodium oleate, polymerised at 30°, and the resulting duprene then coagulated by means of dilute acetic acid (B.P. 387340, Du Pont de Nemours & Co.). Owing to the speed with which polymerisation takes place it is desirable to add inhibitors such as dihydroxybenzenes, etc., and solvents, to retard the polymerisation, and it is also necessary to add plasticisers, etc., to assist in working the product (B.P. 387363, Du Pont de Nemours & Co.).

α-Chloro-butadiene may also be polymerised to a rubber-like product by treating with benzoyl peroxide at 25°, or with metallic sodium at room temperature (B.P. 421146, I.G. Farbenindustrie A.-G. ; *see also* B.P. 389122, Du Pont de Nemours & Co.).

The chlorination of hydrochlorides of vinylacetylene is dealt with by Berchet and Carothers in recent papers (J. Amer. Chem. Soc. 1933, **55**, 1628, 2004), and the polymerisation of alkyl-substituted chloroprenes by Carothers and Jacobson (*ibid.* 1624). βγ-Dichloro-$\Delta^{\alpha\gamma}$-butadiene (b.p. 39°–41°/80 mm. ; 98°/760 mm.) polymerises even more readily than chloroprene but the opaque non-plastic product is devoid of rubber-like properties (Berchet and Carothers, *l.c.*).

Other patents dealing with the polymerisation of chloroprene are : B.P. 421435 (de Holczer and New York Belting and Packing Co.) ; U.S.P. 1967865 (Collins and Du Pont de Nemours & Co. ; *see also* Bridgwater and Krisman, Ind. Eng. Chem. 1932, **24**, 280).

The corresponding bromo compound, *Bromoprene*, has also been prepared by treating vinylacetylene with concentrated hydrobromic acid in presence of cuprous bromide ;it forms a slightly greenish oil, b.p. 42°–43°/165 mm. ; δ-bromo-$\Delta^{\alpha\beta}$-butadiene is first formed :

$$CH_2:CH{\cdot}C\vdots CH \rightarrow CH_2Br{\cdot}CH:C:CH_2 \rightarrow CH_2:CH{\cdot}CBr:CH_2$$

(b.p. 109°–111°/760 mm.) and rapidly isomerises to bromoprene (Berchet, Carothers, Collins, and Kirby, J. Amer. Chem. Soc. 1933, **55**, 786–789, 2807). Bromoprene also polymerises readily to form a synthetic rubber.

By the action of δ-chloro-$\Delta^{\alpha\beta}$-butadiene upon alkyl magnesium halides β-alkyl-$\Delta^{\alpha\gamma}$-butadienes are obtained ; thus *isoprene* may be obtained from δ-chloro-$\Delta^{\alpha\beta}$-butadiene and methyl magnesium iodide, but the yields are poor (Berchet and Carothers, J. Amer. Chem. Soc. 1933, **55**, 2813).

Klebanski, Zurich, Dolgopolski, *et alia* (Bull. Acad. Sci. U.R.S.S. 1935, **9**, 189) have shown that in presence of mercuric sulphate, or mercuric oxide + boron fluoride, vinylacetylene condenses with formic acid to yield β-formyl-$\Delta^{\alpha\gamma}$-butadiene, *formoprene*,

$$CH_2:C(O{\cdot}CHO){\cdot}CH:CH_2,$$

b.p. 42°/40 mm. : this also polymerises in a few days to form a rubber-like mass, *Sovprene* (*Sovoprene*).

Divinyl acetylene.—As already noted, on passing acetylene into a concentrated cuprous chloride-ammonium chloride solution, there is formed in addition to vinylacetylene, considerable amounts of *divinylacetylene*,

$$CH_2 : CH{\cdot}C \vdots C{\cdot}CH : CH_2,$$

b.p. 83·5°/760 mm., and unless the vinylacetylene is rapidly removed from the reaction mixture, the divinyl-compound becomes the main product :

$$CH_2 : CH{\cdot}C \vdots CH + CH \vdots CH \rightarrow CH_2 : CH{\cdot}C \vdots C{\cdot}CH : CH_2$$

(*cf.* Carter, Downing, Calcott, and Nieuwland. J. Amer. Chem. Soc. 1931, **53**, 4197 ; B.P. 384654–5, Du Pont de Nemours & Co. ; and previous general references under vinylacetylene). By spontaneous uncontrolled polymerisation, alone or dissolved in a mixture of solvents, divinylacetylene polymerises to a white or yellowish polymer that is spontaneously and highly explosive In presence of excess water, with small amounts of ammonia and some copper salt, the polymer when finely divided resembles cuprene and is non-reactive ; it consists possibly of tritolylene. Hydrochloric acid with cuprous chloride gives with divinylacetylene a product that so far has not been isolated owing to the rapidity with which it polymerises (Nieuwland, Ind. Eng. Chem. 1935, **27**, 853). With 12N-HCl and cuprous chloride at 0°–15°C., divinylacetylene gives *$\alpha\gamma$-dichloro-$\Delta^{\beta\delta}$-hexadiene*, b.p. 80°–82°/17 mm. (Coffmann, Nieuwland and Carothers, J. Amer. Chem. Soc. 1933, **55**, 2048). Vinylacetylene gives with chlorine in carbon tetrachloride at −50° *$\alpha\delta$-dichloro-$\Delta^{\beta\gamma\epsilon}$-hexatriene*, b.p. 45°–46°/3 mm., and with chlorine at 5°-10°C. *$\alpha\gamma\delta\zeta$-tetrachloro-$\Delta^{\beta\delta}$-hexadiene*, b.p. 84°–89°/2 mm. (Coffmann and Carothers, J. Amer. Chem. Soc. 1933, **55**, 2040). In B.P. 389122, Du Pont de Nemours & Co. claim the production of a series of halogenated products varying from liquids to brittle solids by chlorinating divinylacetylene, 1 : 2 : 3 : 4 : 5 : 6-*hexachlorohexene*-3 being claimed as one end product. With thiocresol and divinylacetylene in ultra-violet light there is formed *$\alpha\zeta$-di-p-tolylthiol-Δ^{γ}-hexinene*, m.p. 74·5°–75·5° (Carothers, J. Amer. Chem. Soc. 1933, **55**, 2008).

Divinylacetylene is so reactive that it is difficult to apply successfully the catalysts used for acetylene in the preparation of derivatives. Sulphuric acid, 60 to 70%, with subsequent hydrolysis, produces the highly unsaturated compound, *vinyl allyl ketone*. The mercury catalyst is immediately destroyed on contact with divinylacetylene. Using calcium chloride with a little water as a catalyst, and passing in air, divinylacetylene yields formaldehyde together with a polymer of unknown structure. By controlled polymerisation a synthetic drying oil ("S.D.O.") is obtained which has remarkably resistant properties as a lacquer film ; it is not attacked by 60% sulphuric acid, bromine, chlorine, or any known organic solvent (Nieuwland, Ind. Eng. Chem. 1935, **27**, 853 ; Du Pont de Nemours & Co., B.P. 384655).

Although divinylacetylene is prepared from acetylene by an exothermic reaction, it has probably the lowest heat of formation of any known hydrocarbon, about −160,000 g.-cal. (Nieuwland, *l.c.*). For reactions of substituted divinylacetylenes, *see* Blomquist and Marvel (J. Amer. Chem. Soc. 1933, **55**, 1655) ; for a discussion of the structures of the thermal polymers of divinylacetylene, *see* Carothers and Cupery (*ibid.* 1934, **56**, 1167).

(*d*) **Vinyl Halides and Esters, etc.**—During recent years considerable attention has been paid to the technical investigation of vinyl compounds, other than vinylacetylene and divinylacetylene, as under suitable conditions acetylene readily forms vinyl halides, esters, ethers, etc., which can be polymerised to form useful resinous or plastic substances. *Mowilith H* and *N*, for instance, being colourless or pale yellow polymerisation products of vinyl acetate, polymerisation in light occurring more rapidly in nitrogen than in oxygen. Polyvinyl ester resins are made by Shawinigan, Ltd., under the name of *Gelva* and *Alvar* products. In the United States a polymerised mixture of vinyl chloride and vinyl acetate is extensively used under the name of *Vinylite*, particularly for gramophone records and similar material. The question of polymerisation of vinyl compounds is discussed by Staudinger and Schwalbach (Annalen, 1931, **488**, 8) and by Davidson and McClure (Ind. Eng. Chem. 1933, **25**, 645).

(i) *Vinyl Halogen Derivatives.*—Vinyl halides are prepared by heating together acetylene hydrocarbons with halogen hydrides or methyl halides, under pressure, acetylene and hydrochloric acid yielding *vinyl chloride* ; acetylene and methyl chloride affording, presumably, $CH_3{\cdot}CH{=}CHCl$ (Traun's Forschungslab. B.P. 156117). The same inventor claims also the production of vinyl chloride by adding calcium carbide to hot concentrated hydrochloric acid containing mercuric ethylenechlorosulphonate ; organic solvents may replace the water, and copper, tin, aluminium, or zinc replace the mercury ; ethylidene chloride and dichloracetaldehyde are formed as by-products (B.P. 156120). According to B.P. 339093 (Consort. f. Elektrochem. Ind. G.m.b.H.) acetylene and hydrogen chloride are passed over active carbon or silica gel containing a catalyst such as bismuth chloride, at 180°–240°, to give vinyl chloride ; salts of a number of metals are noted as suitable catalysts. In a similar process (I.G. Farbenind. A.-G., B.P. 339727) the reaction is effected at 180°, using active carbon containing residual phosphoric acid ; or, again, the carbon catalyst may be pre-treated with hydrogen halide at a temperature higher than that of the subsequent reaction (Baxter and Imperial Chemical Industries, B.P. 349017). The production of vinyl chloride from acetylene and dry hydrogen chloride in presence of stannic chloride and a trace of mercuric chloride, or alternatively, in presence of aqueous hydrochloric acid, cuprous chloride, and calcium chloride, is claimed in U.S.P. 1926638, 1934324 (Carbide and Carbon Chem. Corp.) ; or a solution of a cuprous salt in presence of ammonia (or an amine) may be utilised (Du Pont de

Nemours & Co., B.P. 384654). Wibaut and Dalfsun found that acetylene reacts smoothly with hydrogen chloride at 25°–195° in presence of mercuric chloride upon silica gel, to form vinyl chloride; the presence of zinc chloride catalysed the addition of a further molecule of hydrogen chloride to give $CH_3{\cdot}CHCl_2$ (Rec. trav. chim. 1932, **51**, 636; 1934, **53**, 489).

Alternatively, vinyl chloride may be prepared from ethylene dichloride by treatment with methyl alcoholic alkali, by the classical method (I.G. Farbenindustrie A.-G., B.P. 349263). Ethylene dichloride, diluted with steam, hydrochloric acid, nitrogen, or carbon dioxide decomposes at 800°–1,000° to give vinyl chloride and acetylene; a short period of heating (0·8 to 2·0 seconds) favours the formation of vinyl chloride, whilst longer heating (2 to 6 seconds) and higher temperatures favour the formation of acetylene (Baxter, Edwards, Winter, and Imperial Chemical Industries, Ltd., B.P. 363009). Vinyl chloride may also be obtained by heating *ααβ*-trichloroethane with finely divided zinc, iron, or aluminium at 50°–60° in presence of water, *e.g.* by heating with an aqueous suspension of zinc dust at 50°–60°, or by passing with steam over iron filings at 300°C. (I.G. Farbenindustrie A.-G., B.P. 352842).

The production of $\Delta^{\alpha\gamma}$-*butadiene* from vinyl halides by passing the vapour of the latter through molten lead or tin is claimed in B.P. 329748 (Leyes).

In B.P. 299319 the I.G. Farbenind. A.-G. describe the formation of chloroacetaldehyde, with a yield of 75%, by introducing chlorine and vinyl chloride into water at 0°–40°. At higher temperatures chloroacetic acid is formed; trichloroethane also tends to be produced in presence of light; in B.P. 299722 the chloroacetaldehyde is separated by passing in hydrogen chloride until a concentration of 20% is reached and then separating the products by distillation.

The production and properties of *vinyl bromide* are discussed by Wibaut *et alia* (Rec. trav. chim. 1931, **50**, 313, 1021), and by Burkhardt and Cocker (*ibid.* 837). The preparation of *vinyl iodide* is dealt with by Emschwiller (Compt. rend. 1933, **196**, 1028).

Polymerisation Products. — A polymer soluble in chlorobenzene and insoluble in acetone is obtained by exposing gaseous vinyl chloride or its solution in an organic solvent to ultraviolet light; a soluble lead salt may be used as a catalyst, and the products separated by means of acetone (van Dyke, B.P. 255837; Osstromislensky and van Dyke, B.P. 260550). According to Du Pont de Nemours & Co. (B.P. 319587, 319591) vinyl chloride may be polymerised either (*a*) in a solvent by means of ozone and heat (90°–120°), or by the action of light; or (*b*) a solution of vinyl chloride and benzoyl peroxide in chlorobenzene may be heated to 118° by passage through a tin-lined tube, and rapidly cooled to yield chiefly the α-polymer, soluble in toluene. Polymerisation may also be effected by heating a vinyl halide under pressure in a solvent at 30°–60° and in presence or absence of a catalyst, with or without exposure to active radiation, the product being a glassy substance similar to celluloid (I.G. Farbenind. A.-G., B.P. 313569). The use of polymerised vinyl chloride or esters as a binding material in plastic or coating compositions is referred to by the same firm in B.P. 349100.

Modifications of the method of polymerisation are given by I.G. Farbenind. A.-G. in B.P. 358534, 385004, 387736, whilst in B.P. 410132 the same firm refers to the polymerisation of an aqueous emulsion of vinyl chloride by irradiation or the use of a peroxide catalyst, followed by coagulation with an acid.

For certain purposes it is an advantage to obtain a mixed polymer from vinyl chloride and vinyl acetate, by conjoint polymerisation of a mixture containing at least 70% of the halide and not more than 30% of the ester, in presence of benzoyl peroxide (Carbide and Carbon Chem. Corp., B.P. 388309), by the use of acetylbenzoyl peroxide (B.P. 397364), or in presence of a suitable organic solvent (B.P. 406338; *cf. also* I.G. Farbenind. A.-G., B.P. 396186). The production of plastic masses by further chlorination of polyvinyl halides is the subject of B.P. 401200 (I.G. Farbenind. A.-G.). Dreyfus causes vinyl halides to react with hydroxy compounds such as glycol to produce, for example, *glycol vinyl ether*, which is then polymerised (B.P. 398173). In the same way vinyl chloride may be condensed with phenols, in presence of aluminium or ferric chlorides, to produce *vinyl phenols*, which are then suitably polymerised (British Celanese Co., B.P. 409132). The polymerisation of vinyl compounds under pressures of not less than 2,000 atm. is proposed by Bridgeman, Conant, and Du Pont de Nemours & Co. (U.S.P. 1952116).

Simon (U.S.P. 1929453) has shown that completely polymerised vinyl halides form rubber-like gels with suitable plasticisers such as tricresylphosphate, and the product is marketed as "Koroseal" plastic. It can be processed on hot-mill rollers and is specially suited for use with oils. It is stated to age much less with light and weather than natural rubber (*cf. also* Brous and Simon, Ind. Eng. Chem. 1935, **27**, 667; Carothers, *ibid.* 1934, **26**, 30; Katz and Whitby, *ibid.* 1933, **25**, 1204; Osstromislensky, Canad. Pat. 270225).

(ii) *Vinyl Esters and Ethers.*—On passing acetylene into a carboxylic acid in presence of suitable catalysts, in particular of mercury salts, there are formed successively (in the case of acetic acid) *vinyl acetate* and *ethylidene diacetate*:

$$CH{:}CH + CH_3{\cdot}COOH = CH_3{\cdot}CO{\cdot}O{\cdot}CH{:}CH_2$$

$$CH_3{\cdot}CO{\cdot}O{\cdot}CH{:}CH_2 + CH_3{\cdot}COOH = (CH_3{\cdot}CO{\cdot}O)_2CH{\cdot}CH_3$$

(Traun's Forschungslaboratorium, B.P. 156117).

In presence of excess of acid and with prolonged treatment the main product is ethylidene diacetate, which may be utilised for the production of acetic anhydride (*see* ACETALS). In B.P. 231841 (Consort. f. Elektrochem. Ind. G.m.b.H.) the process is modified by circulating acetylene continuously, the vinyl acetate distilling off as it is formed. Its manufacture is now an important industrial process, as the ester, in common with other vinyl compounds, readily polymerises to form valuable resins.

A description of the Shawinigan process for manufacturing vinyl acetate (and ethylidene diacetate) is given by Morrison and Shaw (Amer. Electrochem. Soc., May 11, 1933 ; *cf.* Chem. Trade J. 1933, **92**, 415). In this plant acetylene reacts with acetic acid at about 35°C. in presence of a mercuric sulphate catalyst prepared by precipitation from acetic acid solution with sulphuric acid. The plant (1933) had a capacity of 2 tons vinyl acetate daily and included : (i) a unit for making the catalyst, a reaction kettle, and a unit for circulation of the acetylene ; this system remains the same for the production of vinyl acetate, ethylidene diacetate, or both ; (ii) the vinyl acetate system, consisting of a continuous still for separating the total condensate into recovered acetic acid and crude vinyl acetate ; (iii) the ethylidene diacetate system, which handles the reaction kettle mixture, removes the mercury sludge, and separates crude ethylidene diacetate. If vinyl acetate is the only product required, the system can be modified so that the crude ethylidene diacetate is hydrolysed and the acetic acid returned to the kettle ; (iv) the mercury recovery system, consisting of a simple distillation furnace (*cf.* Skirrow, Morrison, and Canadian Electro Products, Ltd., B.P. 308169, 308170, 335223).

Vinyl acetate is a colourless inflammable liquid, b.p. 73°C., which polymerises readily under the influence of light, heat and peroxide catalysts to form resins of high molecular weight.

It is also possible to synthesise vinyl acetate by a vapour-phase method at 180°–250°, by passing acetic acid vapour and acetylene, in proportions of 1 : 9, over a catalyst consisting of zinc or cadmium acetate or phosphate, on active carbon (Ushakov and Feinstein, Ind. Eng. Chem. 1934, **26**, 561).

The Consort. f. Elektrochem. Ind. G.m.b.H. in B.P. 285095 pass a mixture of equal volumes of acetylene and acetic acid vapour rapidly over zinc or cadmium acetate mounted on a carrier, at 210°–250°C. ; *e.g.* a mixture of 4 to 5 cu. m. of acetylene and 5 kg. of acetic acid vapour yields a product containing 13–16% of vinyl acetate, an output of 0·5–0·7 kg. of ester being obtained per hour. E. I. Du Pont de Nemours & Co. pass acetylene in excess into acetic acid containing mercuric sulphate and diluted with kerosene, at 70°–90° ; 11–15% of vinyl acetate is obtained at each distillation. *Vinyl propionate*, b.p. 90°–100°C., and *vinyl butyrate*, b.p. 115°–120°C., are prepared in a similar manner using the corresponding acids (B.P. 319589).

The same patentees claim a 70 to 85% yield of vinyl acetate by the interaction below 50°C. of acetylene with acetic acid and acetic anhydride, in presence of sulphoacetic acid and mercuric and ferric sulphates (B.P. 379705). Imperial Chemical Industries, Ltd., pass acetylene into a lower aliphatic monocarboxylic acid, below 50°C., in presence of acetic anhydride, sulphoacetic acid, and a mercury catalyst, sodium acetate being finally added and the vinyl ester distilled off under diminished pressure (B.P. 351318).

The process is rendered less hazardous by using as a catalyst the mercury salt of an organic sulphonic acid such as methionic acid or benzenedisulphonic acid at a temperature between 30°–100°C. (Boehringer and Soehne, B.P. 427448). Vinyl esters of carboxylic acids containing more than 5 carbon atoms may be prepared from acetylene and suitable acids in presence of zinc or cadmium salts at 160°–185°C. and 5–25 atm. pressure ; the following *esters* have been prepared : the n-*valerate*, b.p. 135°, the *octoate*, b.p. 94°/12 mm., the *palmitate*, b.p. 165/2 mm., the *oleate*, b.p. 173°/2 mm., and the *β-naphthoate*, b.p. 153°/4 mm. (I.G. Farbenind. A.-G., B.P. 395478).

Vinyl formate may be obtained by heating a higher ester with formic acid, a mercury salt of an inorganic acid, such as phosphoric acid, and an anti-oxidant such as a dihydroxybenzene ; under such conditions, for instance, vinyl acetate yields vinyl formate (I.G. Farbenind. A.-G., B.P. 425673).

A different process altogether for the production of vinyl esters is to heat acetaldehyde, or better, paraldehyde, with an organic acid anhydride (*e.g.* acetic anhydride) in presence of 0·25–2·0% of sulphuric acid, phosphoric acid, or toluene-*p*-sulphonic acid, and fractionally distil the products (Perkins and Carbide and Carbon Chem. Corp., B.P. 418943).

Dihalogen ethyl esters, such as α-β-dichlorethyl acetate, are obtained by direct halogenation of the corresponding vinyl esters at 0°C. in presence of a diluent (Soc. des Usines Chim. Rhône-Poulenc, B.P. 325115), and on heating this with zinc chloride (B.P. 329721), or by passage through tubes containing kieselguhr or pumice carrying an acidic substance, the acetate is broken down into *acetyl chloride* and *chloroacetaldehyde* (Soc. des Usines chim. Rhône-Poulenc, B.P. 330511).

Under similar conditions α-chloroethyl acetate at 250°–300°C. yields acetyl chloride and acetaldehyde (*see also* Ellis, " Chemistry of Synthetic Resins," Vol. II, p. 1016, New York, 1935).

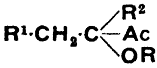
Vinyl ethers may be obtained by a variety of methods from acetylene. In B.P. 156121 (Traun's Forschungslaboratorium) acetylene is forced under pressure into concentrated sulphuric acid below 0°C., in presence of mercuric sulphate, the product being *vinyl sulphuric acid* ; on heating this acid with an alcohol under pressure alkyl-vinyl ethers are formed, *e.g.* *vinyl ethyl ether*, $CH_2{=}CH{\cdot}O{\cdot}C_2H_5$, and it may also be formed directly by passing acetylene under pressure into a cold mixture of ethyl alcohol and concentrated sulphuric acid (*cf.* Miyamoto, J. Chem. Soc. Japan, 1922, **43**, 21). B.P. 231841 (Consort. f. Elektrochem. Ind. G.m.b.H.) describes the production of *vinyl ether* by introducing acetylene into an emulsion of mercuric phosphate in absolute alcohol and ligroin. Mixed vinyl ethers may be obtained by the action of acetylene upon various liquid monomeric hydroxy compounds (such as methanol, ethanol, *n*-butanol, glycol, phenol, etc.) in presence of alkaline condensing agents, with or without a mercury compound (I.G. Farbenind. A.-G., B.P. 369297). Again, vinyl ethers may be produced by passing the vapour of an acetal over silver, gold or a metal of the platinum or palladium group, with the addition, if desired, of other substances; thus diethyl acetal over palladinised asbestos at 270°C. yields vinyl ethyl ether, di-*n*-butyl acetal at 300° yields *vinyl* n-*butyl ether* (I.G. Farbenind. A.-G., B.P. 345253). More complex vinyl ethers may be prepared by allowing vinyl monohalides to react with alkali alkoxides or phenates, in presence of suitable diluents such as alcohol or benzene; thus β-chloro-Δ^{β}-butylene with alkali ethoxide affords *ethyl* 1 : 2-*dimethylvinyl ether* (I.G. Farbenind. A.-G., B.P. 332605). The preparation of vinyl ethyl ether, vinyl butyl ether and vinyl *m*-cresyl ether by a similar method is described by the same firm in B.P. 341074.

Alkyl or aryl vinyl ethers may also be prepared by the action of acetylene upon suitable hydroxy compounds (alcohols or phenols) at 80°–250°C., in presence of alkaline condensing agents such as oxides, hydroxides or cyanides of alkali metals, alkaline earth metals, etc. (I.G. Farbenind. A.-G., B.P. 369297, 427036).

The process is further modified in B.P. 430764, by allowing acetylene to interact with monohydric alcohols at atmospheric pressure, employing sufficient alkaline catalyst to raise the boiling-point of the mixture to the requisite temperature; thus, a solution of caustic potash (15 parts) in *n*-butyl alcohol (100 parts), boiling at 126°, is caused to run down an absorption tower up which a stream of acetylene is ascending, at such a rate that the level remains constant, due to the removal by distillation of the resulting *vinyl* n-*butyl ether*, b.p. 91°–95°C.

Mitchell and Imperial Chemical Industries, Ltd. (B.P. 428080) cause acetylene to react with aliphatic alcohols or phenols, in presence of freshly precipitated mercuric sulphate in absence of mineral acid.

By the treatment of vinyl ethers with organic or non-oxidising inorganic acids in presence of catalysts such as boron trifluoride, sulphuric acid, hydrochloric acid, thionyl chloride, etc., in a suitable diluent, if necessary at a raised temperature and pressure, there are obtained ethylidene-alkyl or aryl-ethers of the general formula



$$R^1\cdot CH_2\cdot C\begin{cases}R^2\\ Ac\\ OR^3\end{cases}$$

For instance, vinyl ethyl ether treated with hydrogen chloride at 0° yields *α-chloro-diethyl-ether*, b.p. 92°–95°C.; vinyl ethyl ether with glacial acetic acid yields *acetic(ethoxyethylidene)-ester*, etc. (I.G. Farbenind. A.-G., B.P. 352070). The Chemische Forschungs Ges., in B.P. 434580, claim to obtain *vinyl alcohol* itself by cautious hydrolysis of mono-vinyl esters or ethers with acid or alkali at low temperatures, *e.g.* 20°C., followed by ether extraction and vacuum distillation.

The production of *methyl vinyl ketone* by hydration of vinyl acetylene has already been referred to (p. 88). The production of other vinyl ketones, *e.g.* $CH_2\cdot CO\cdot C(:CH_2)\cdot CH_2\cdot OH$, is referred to in B.P. 389884 (I.G. Farbenind. A.-G.); such substances may be obtained by the distillation in presence of dehydration catalysts of the *αα*-dimethyl-ketones of B.P. 381686 and 361597; for example, *αα*-dimethyl-acetone from acetone and formaldehyde on distillation *in vacuo* with phosphoric acid, alumina, or aluminium phosphate yields the product $CH_3\cdot CO\cdot C(:CH_2)\cdot CH_2\cdot OH$ referred to above (*see also* Ellis, "Chemistry of Synthetic Resins," Vol. II, p. 1007, New York, 1935).

Polymerisation Products of Vinyl Esters and Ethers.—These have attained considerable importance owing to the valuable properties of the products as components of resins, lacquers, moulding powders, etc. Resinous products are formed by the interaction of an aliphatic vinyl ester and a saturated aliphatic aldehyde; *e.g.* vinyl acetate and acetaldehyde, or vinyl formate and acetaldehyde, or vinyl butyrate and butyraldehyde are heated under pressure (Matheson, Skirrow, and Canadian Electro Products, Ltd., B.P. 280246, 295322). In B.P. 294474 the I.G. Farbenind. A.-G. claim the production of rubber-like masses by polymerising vinyl esters of organic acids or vinyl ethers, and incorporating solid nitrogenous compounds such as proteins, peptones, etc., or solid hydrocarbons such as naphthalene; for example, vinyl acetate is emulsified with casein and then vulcanised in ultra-violet light; or naphthalene is dissolved in vinyl acetate, benzoyl peroxide is added, and vulcanisation completed by ultra-violet radiation. In G.P. 506148 the same firm modify the character of polymerised vinyl esters by incorporating natural resins or oils, whilst in U.S.P. 1768434 Blaikie and Canadian Electro Products, Ltd., claim that the addition of 0·1% of sulphur to vinyl compounds prevents polymerisation during distillation or storage and inhibits their condensations with aldehydes. Du Pont de Nemours & Co. in B.P. 319587 claim the polymerisation of vinyl acetate by the methods adopted for vinyl chloride (*v. supra*). Polymerisation of vinyl esters and halides may be effected in an ozonised solvent (*e.g.* ozonised ethylene dichloride) (B.P. 319587), or they may be polymerised by forcing a solution of the vinyl compound and a catalyst such as benzoyl peroxide successively through heated and cooled tubes (B.P. 319588); or by heating a solution of vinyl acetate to 85°–100°C. a polymer is obtained which does not "cobweb" on spraying (Du Pont de Nemours & Co., B.P. 319590). An apparatus suitable for effecting the polymerisation of vinyl compounds is described in B.P. 331265 (I.G. Farbenind. A.-G.). The addition of a small amount of a base, such as *cyclo*hexylamine, in the preparation of polymerised vinyl esters, is recommended in B.P. 336237 (I.G. Farbenind. A.-G.). The use of "per" salts such as peroxides, perborates or persulphates for effecting polymerisations is claimed in B.P. 353866 by the same firm. Plastic masses can be prepared by polymerising a mixture of a vinyl ester or ether with other polymerisable bodies such as acrylic ethyl ester, isoprene, etc., in absence of a solvent (I.G. Farbenind. A.-G., B.P. 357173). Vinyl acetate may be polymerised in a solvent such as gasoline or benzene, which dissolves the ester but not the polymer (Imperial Chemical Industries, Ltd., B.P. 366897). By heating polymerised vinyl alcohol, ester, or ether to 100°C., in presence or absence of a catalyst such as hydrochloric acid, lactic acid, or zinc chloride, insoluble and infusible products are obtained (I.G. Farbenind. A.-G., B.P. 322157). Again, various types of condensation products are obtained by treating polymerised vinyl alcohols with an aliphatic aldehyde such as formaldehyde, in presence of acid catalysts (I.G. Farbenind. A.-G., B.P. 337806). Partially or completely hydrolysed vinyl esters or their polymers may be combined with aliphatic aldehydes ; thus dry polymerised vinyl acetate is hydrolysed by heating with dilute hydrochloric acid, and the product then condensed with formaldehyde (Blaikie, Morrison, Skirrow, and Canadian Electro Products, Ltd., B.P. 351082). Polymerised vinyl derivatives may be incorporated with unvulcanised rubber and the mixture then vulcanised (Soc. des Usines Chim. Rhône-Poulenc, B.P. 353194). Highly viscous solutions can be prepared by treating aqueous solutions of a polyvinyl alcohol with formaldehyde or acetaldehyde, etc., under mild conditions (I.G. Farbenind. A.-G., B.P. 356408). Condensation products of a polyvinyl alcohol with aldehydes, urea, phenol casein, etc., are claimed in B.P. 361910 by the same patentees. Hydroxyalkyl polyvinyl compounds are obtained by condensing an alkylene oxide, such as ethylene oxide, with a polyvinyl alcohol (B.P. 364323, 368530), whilst the reduction of polymeric vinyl ketones to polymeric alcohols and subsequent condensation with aldehydes to form plastic masses is claimed in B.P. 369313 by I.G. Farbenind. A.-G. The condensation of polymerised vinyl chloroacetate with alkali alkoxides and phenates to form synthetic resins is claimed in B.P. 364400 (Imperial Chemical Industries, Ltd.). Polymerised vinyl esters may be purified by washing with cold water (B.P. 319682) or by treatment with hot solvents such as toluene, butyl alcohol, etc. (I.G. Farbenind. A.-G., B.P. 313912).

Adsorbent materials such as Florida earth, carbon, kieselguhr, etc., can be used for polymerising vinyl ethers (I.G. Farbenind. A.-G., B.P. 379694). In the polymerisation process the amount of acid present is kept below the equivalent of 1% of hydrochloric acid to obtain good coloured products (Du Pont de Nemours & Co., B.P. 384639).

The following further processes may be noted : aldehyde resins are fused with polymers of vinyl compounds (Consort. f. Elektrochem. Ind. A.-G., B.P. 314399) ; tricresyl phosphate or other plasticisers are added to polymerised vinyl compounds to improve their insulating properties (Moss and British Celanese Co., Ltd., B.P. 372327) ; details of the polymerisation process are given in B.P. 381693 (I.G. Farbenind. A.-G.) ; polyvinyl alcohols (obtained by hydrolysis of the esters) are condensed with formaldehyde (Rheinisch-Westfälische Sprengstoff-A.-G., B.P. 383045) or with *cyclo*hexanone (I.G. Farbenind. A.-G., B.P. 383764) ; partially hydrolysed vinyl esters may be used for sizing yarns, etc. (Dreyfus, B.P. 386005, 385978). Special uses of polyvinyl esters for paper coating, as a bonding material in the manufacture of ply-wood, etc., are given in B.P. 389914 (Reichl) and in B.P. 389988 (Carbide and Carbon Chem. Corp., Ltd.).

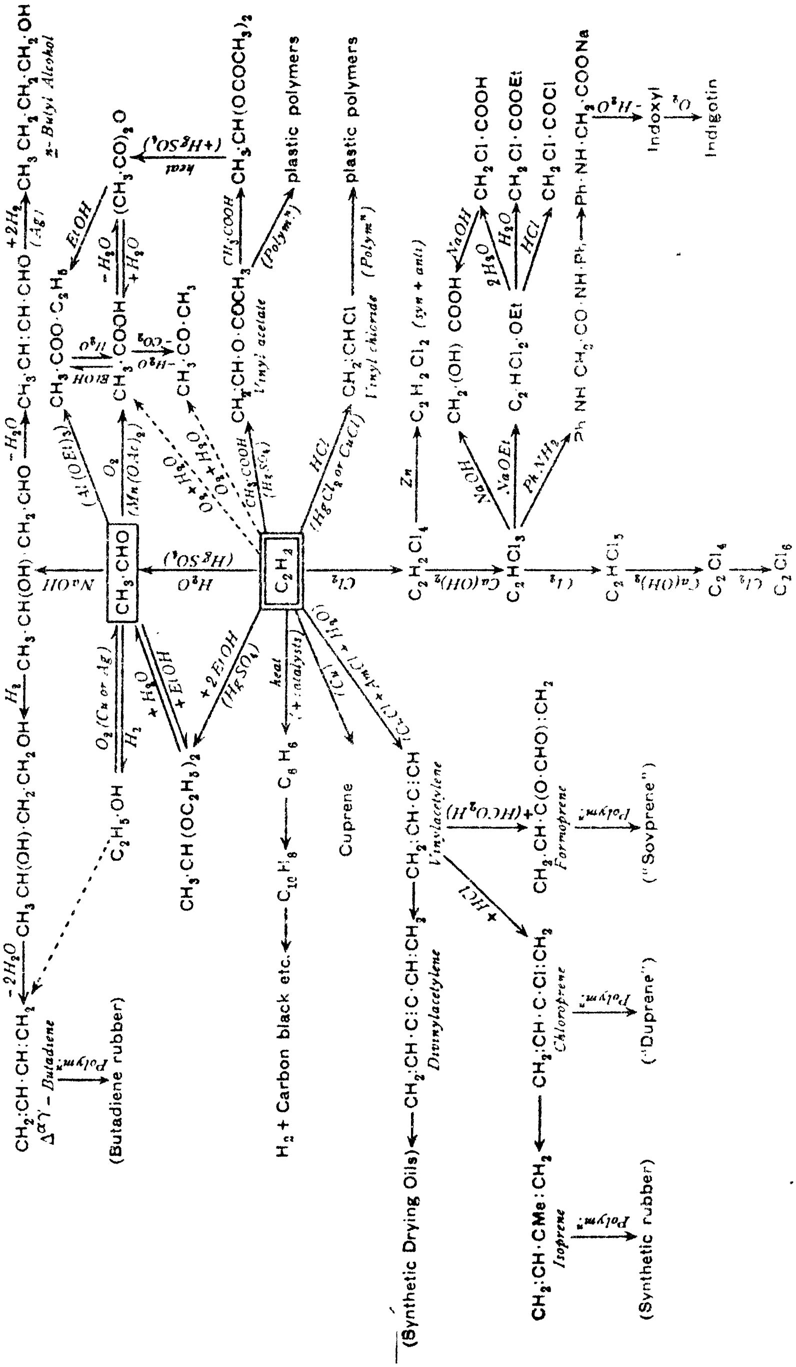
I.G. Farbenind. A.-G. claim the following :— vinyl ethers are polymerised by heating with practically anhydrous inorganic reagents such as aluminium chloride, ferric chloride, zinc chloride, etc., or mineral acids, in very small amounts— 0·001 to 5·0% of weight of ether (B.P. 378544) ; mixtures of vinyl halides, esters, ethers, etc., which may be mixed with other polymerisable substances such as styrene, are heat-polymerised so that any substantial auto-polymerisation is avoided (B.P. 381693) ; polyvinyl alcohols are condensed with aldehydes to produce plastic products (B.P. 403750) ; polymerised vinyl alcohols and esters are used to improve the properties of hydrocarbon lubricants, paraffin wax, etc. (B.P. 413624 (void), 413637).

Catalysts for the polymerisation of vinyl compounds may be prepared by heating together an alkali per-salt with an organic acid anhydride, *e.g.* sodium perborate with acetic anhydride (Blaikie and Canadian Electro Products, B.P. 387323, 387335). Vinyl esters may be polymerised by heat in presence of a catalyst and a controlled quantity of diluent ; for instance, vinyl acetate is heated with sodium perborate, acetic anhydride, and toluene (Blaikie, Morrison, Shaw, and Canadian Electro Products, Ltd., B.P. 387353) ; partially hydrolysed polyvinyl acetate is condensed with an aldehyde, such as acetaldehyde, in presence of a peroxide catalyst, to produce “ secondary resins ” (Skirrow and Whyte, B.P. 405986) ; polyvinyl esters are used for impregnating inert materials for moulding purposes (Canadian Electro Products, Ltd., B.P. 416413).

The use of a mixture of polyvinyl acetate with a plasticiser for the manufacture of laminated glass is referred to in B.P. 403723 (Renfrew, Fleming, and Imperial Chemical Industries, Ltd.). Polyvinyl esters may be condensed with acetals in presence of a trace of acid, to produce plastic masses (Bevins, Jones, Renfrew, and Imperial Chemical Industries, Ltd., B.P. 404279), and similarly polyvinyl esters may be caused to react with ethylidene diacetate in presence of absolute alcohol and a trace of an acid catalyst such as hydrogen chloride (*idem*, B.P. 407050). The production and utilisation of vinyl propionate, phthalate, etc., is claimed in B.P. 308657–8–9 (Celluloid Corporation, Walsh, and Caprio).

Very little has been published regarding the properties of the polymerised vinyl esters, but the following typical data regarding “ Gelva ” and “ Alvar ” products (Shawinigan, Ltd.) will indicate the general properties of these bodies. Solubility of “ Gelva 20 ” in solvents at 20°–25°C. : butyl alcohol, 0·0% ; *cyclo*hexanol, 11·4% ; *iso*-propyl alcohol, 0·03% ; acetal, 2·2% ; benzyl benzoate, 16·2% ; dibutyl phthalate, 8·7% ; ligroin, gasoline, heavy paraffin, ethyl ether, carbon disulphide, oleic acid, less than 1·0%. The viscosity of various solutions of “ Gelva 20 ” in 10% concentration (water=1) is : benzene, 2·8 ; benzyl alcohol, 31·4 ; acetone, 11·4 ; aniline, 32·3 ; chloroform, 11·7 ; tetrachloroethane, 40·0 ; acetic acid, 7·8 ; lactic acid, 323·0 ; ethyl acetate, 2·0. The softening points of the "Gelvas" vary from about 103° to 143°C., the refractive index of "Gelva 20" at 20°C. being 1·467. The solubilities of the "Alvars" are similar to those of the "Gelvas," whilst their softening points vary from 136° to 160°. Both types of products possess good electrical insulating properties.

The following diagram may serve to indicate the chief reaction products of technical application obtained from acetylene and acetaldehyde.



VI. Detection and Analysis.

For the detection of acetylene Llorens recommends the use of test papers soaked in a solution of copper sulphate and sodium chloride, decolorised with sodium bisulphite (Anal. Fís. Quím. 1912, **10**, 139 ; 1913, **11**, 320). Weaver (J. Amer. Chem. Soc. 1916, **38**, 352) describes a colorimetric method of estimating acetylene, as also does Schultze (Z. angew. Chem. 1916, **29**, 1, 341). Generally, however, for both detection and analysis use is made of an ammoniacal cuprous chloride solution, containing gelatine as a protective colloid, " Ilosvay's solution " (Ilosvay von Nagy Ilosva, Ber. 1899, **32**, 2698).

The uses and limitations of this method have been discussed by various authors, notably Schultze (Z. angew. Chem. 1916, **29**, 341 ; 1931, **44**, 703), Riese (*ibid.* **44**, 701), Pietsch and Kotowski (*ibid.* 309, 388, 703), Czakó (*ibid.* 1931, **44**, 388), Novotny (Coll. Czech. Chem. Comm., 1934, **6**, 514). In complete absence of sulphuretted hydrogen the reagent can detect about 0·0005 vol. % of acetylene, 0·0078% producing an immediate reddening of the solution. Czakó (*l.c.*) describes a modification of the method whereby the limit of sensitivity is reduced below 0·00025%. Pietsch and Kotowsky (*l.c.*) recommend the use of a copper solution containing ammonia and hydrazine.

An apparatus for determining the amount of acetylene in welding gases is described by Krauss (Azetylen-Wiss. Ind. 1932, **35**, 73).

In admixture with ethylene, etc., acetylene can be estimated by passing the gas through neutral silver nitrate solution and estimating the acid set free according to the equation :

$$C_2H_2+3AgNO_3=C_2Ag_2{\cdot}AgNO_3+2HNO_3$$

(Chavastelon, Compt. rend. 1897, **124**, 1364 ; Ross and Trumbull, J. Amer. Chem. Soc. 1919, **41**, 1180). According to Hoepner, however (Z. Nahr. Genussm. 1917, **34**, 453), this method is unreliable, and more accurate results are obtainable by shaking the gas sample with freshly prepared Ilosvay's reagent, separating the copper acetylide formed, washing with dilute acidified ferric sulphate solution, and titrating with permanganate :

$$Cu_2C_2+Fe_2(SO_4)_3+H_2SO_4$$
$$=2FeSO_4+2CuSO_4+C_2H_2$$

The use of a solution of an organo-mercury-halide in 10% aqueous caustic potash for identification of acetylene and its homologues is described by Spahr, Vogt, and Nieuwland (J. Amer. Chem. Soc. 1933, **55**, 2465, 3728) (*see* page 82).

Microchemical methods for the estimation of acetylene are given by Blacet, MacDonald, and Leighton (Ind. Eng. Chem., Anal. Edition, 1933, **5**, 272).

Literature.—" Das Acetylen, seine Eigenschaften, Herstellung und Verwendung," by J. H. Vogel, Leipzig, 1923 ; " Carbid und Acetylen als Ausgangsmaterial für Produkte der chemische Industrie," by J. H. Vogel and Armin-Schultze, Leipzig, 1924 ; " Chemistry of 'Synthetic Resins,'' by Ellis, New York, 1935.

F. A. M.

ACETYLENE BLACK. A carbon pigment, remarkably free from grit, obtained by exploding a mixture of acetylene gas and air under pressure.

ACETYLENE BLUES, PURE BLUE, SKY BLUE (S.C.I.). Direct azo dyes.

ACETYLENE, CHLORINE DERIVATIVES OF. Acetylene reacts with hypochlorites to form chloracetylenes. The addition of chlorine to acetylene gives tetrachlorethane, which, although of less use as a solvent than formerly, has acquired great importance as the starting point of the series of chlorinated ethylenes and ethanes, di-, tri-, and perchlorethylene, tetra-, penta-, and hexachlorethane. These solvents, particularly trichlorethylene, are finding an increasing use as non-inflammable solvents for grease and fat. The development of the series is as follows : acetylene combines with chlorine to form tetrachlorethane, which reacts with lime to form trichlorethylene or, with a reducing agent, to form dichlorethylene. Trichlorethylene adds on more chlorine to form pentachlorethane, which reacts with lime to give perchlorethylene. Hexachlorethane is formed by complete chlorination of perchlorethylene. The chief physical properties of the series are tabulated in Table I.

Chloracetylene, $CCl{:}CH$ or $C{:}CHCl$. Nef (Annalen, 1897, **298**, 356) and Lawrie (J. Amer. Chem. Soc. 1906, **36**, 489) state that the compound is chloracetylidene, but Blitz (Ber. 1913, **46**, 143) opposes this view and claims that it is chloracetylene. It is usually prepared by heating $\alpha\beta$-dichlorethylene with alkaline mercury cyanide solution and warming the resulting mercury chloroacetylide with alkaline potassium cyanide in hydrogen (Hofmann and Kirmreuther, Ber. 1909, **42**, 4234). Other methods of preparation are to warm trichlorethylene with alcoholic caustic potash, or to boil $\beta\beta$-dichloracrylic acid with baryta (*see* Hofmann and Kirmreuther, *l.c.* ; Wallach, Annalen, 1880, **203**, 88 ; Zincke, Ber. 1890, **23**, 3783 ; V. Meyer, *ibid.* 3783 ; Mourelo and Banus, Anal. Fís. Quím. **9**, 84 ; Sastry, Chem. Zentr. 1916, II, 306).

Chloracetylene is an explosive gas unless sufficiently diluted with hydrogen, depositing carbon on combustion. It is soluble in water and alcohol, forms with bromine $CHBr{:}CBrCl$; and the chloracetylides of silver and mercury can be prepared.

Dichloracetylene, $CCl{:}CCl$, a colourless gas boiling at −50°C., has been obtained by Böeseken and Carrière (Verslag. Akad. Wettenschappen, **22**, 1186) by heating the barium salt of trichloracrylic acid. It may be formed by the treatment of calcium carbide with chlorine (Davidson, J. Amer. Chem. Soc. 1918, **40**, 398), for instance, as an intermediate in the formation of *tolane dichloride* by the reaction of benzene, calcium carbide, and chlorine. The reaction of trichlorethylene and alcoholic caustic potash also gives dichloracetylene. It is said to be formed by the action of sodium hypochlorite on diacetylene at 0°C. in the dark, and by reaction of acetylene and HCl in presence of gaseous

TABLE I.

	Formula.	Mol. wt.	B.p. °C.	M.p. °C.	Density $\frac{15°}{4°}$.	R.I. n^{20}_{D}.	Heat of vaporisation, Cals./gm.	Specific heat, Cals./gm.	Expansion coefficient.	Vapour pressure at 20°C., mm. of Hg.	Dielectric constant ε.
Sym-Dichlorethylene	$C_2H_2Cl_2$										
trans . .		96·92	48·4	−50	1·265	1·4490	71·7	0·27	0·00136	286	3·67
cis . . .			60·3	−80·5	1·291	1·4519	75·0	0·27	0·00127	180	7·55
Trichlorethylene .	C_2HCl_3	131·38	86·7	−73·0	1·471	1·4777	57·24	0·223	0·001193	59·4	3·42
Perchlorethylene .	C_2Cl_4	165·84	120·8	−22·4	1·623	1·5056	50·04	0·216	0·001078	17	2·37
Tetrachlorethane .	$C_2H_2Cl_4$	167·84	146·3	−43·8	1·600	1·4942	55·02	0·268	0·000998	5·1	8·15
Pentachlorethane .	C_2HCl_5	202·30	162·0	−29·0	$1·709\frac{0°}{4°}$	1·5040	43·60	0·266	0·0009097	3·5	3·76
Hexachlorethane .	C_2Cl_6	236·76	185·0	185·0	2·091	—	*ca.* 46	—	—	0·22	—

oxidising agents such as NO_2 or formic acid vapour (Bauer, U.S.P. 1540748).

aaβ-Trichlorethane is obtained by direct addition of vinyl chloride and chlorine in sunlight at 80° or in ultra-violet light at 140°–150° (I.G. Farbenind. A.-G., B.P. 298084), or it may be made from vinyl chloride and chlorine in presence of 1% antimony pentachloride in a suitable solvent (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 314781). It is also formed by reaction of C_2H_2, HCl, and Cl_2 in a restricted space over pumice, coke, etc., impregnated with metallic salts (I.G. Farbenind. A.-G., B.P. 344592, 349097). Chlorine passed into *sym*-dichlorethane in presence of aluminium chloride at 20°–40°C. produces *aaβ*-trichlorethane and also *aaaβ*-tetrachlorethane (Prins, Rec. trav. chim. 1926, **45**, 80).

It is a colourless liquid, m.p. −36·7°, b.p. 113·5°. *d* 1·443 It reacts with sodium in presence of ether to give hydrogen, acetylene, and dichlorethylene (*see* Brunner and Brandenburg, Ber. 1877, **10**, 1497 ; Regnault, J. pr. Chem. 1843 [i], **18**, 82 ; Englan, Bull. Soc. chim. 1887 [ii], **48**, 97 ; Schiff, Annalen, 1883, **220**, 96 ; Meyer and Müller, J. pr. Chem. 1892 [ii], **46**, 174 ; Blitz, Ber. 1902, **35**, 3527 ; Regnault, Ann. Chim. [ii], **69**, 151 ; Kramer, Ber. 1870, **3**, 261 ; Delacre, Compt. rend. 1887, **104**, 1186).

s-Tetrachlorethane. Chlorine is without action on acetylene in the pure state, in the absence of light (Schlegel, Annalen, 1884, **226**, 154). In daylight di- and tetrachlor derivatives are formed in succession (Römer, Annalen, 1886, **233**, 214) and traces of impurities, particularly air, cause violent explosive decomposition with formation of free hydrogen chloride and carbon :

$$C_2H_2+Cl_2=2C+2HCl$$

(*See also* U. Tako, Jap. P. 90708 (1931), in which it is claimed that acetylene and chlorine do not explode even in sunlight, in absence of oxygen, below 100°C.)

This decomposition can be avoided by methods depending chiefly on the introduction of suitable catalysts, such as sodium chloride (Sabanejew, Annalen, 1883, **216**, 241, 262), antimony pentachloride (Berthelot and Jungfleisch, Annalen, Suppl. 1870, **7**, 252), aluminium chloride (Mouneyrat, Bull. Soc. chim. 1898 [iii], **19**, 448 ; Compt. rend. 1898, **126**, 1805). For this reason most of the early patents on the subject deal with the methods of avoiding explosions and producing a smooth reaction with continuous combination of the gases. In practice the use of antimony pentachloride is most usual. The apparatus consists of a vessel fitted with a stirrer and divided into two sections, which, however, allow the liquids in the two compartments to mix. The vessel is partly filled with tetrachlorethane, and acetylene and chlorine are passed separately into the two sections. The solutions of acetylene and chlorine mix and react to form tetrachlorethane, which overflows from the vessel if the process is a continuous one, taking with it a portion of the catalyst, which must be replaced continuously. If the production is not continuous, acetylene and chlorine are fed into the two compartments to react and increase the volume of liquid in the vessel until the catalyst is exhausted. The crude tetrachlorethane is then purified by distillation with steam after neutralising any free acid with lime or chalk. Ferric chloride may also be used as a catalyst in place of antimony chloride. The following older patents and processes may be noted : Askenasy and Mugdan (B.P. 18602, 1904) cause acetylene and chlorine to react in solution in tetrachlorethane, using antimony pentachloride as catalyst. Tompkins (B.P. 19568, 1904) advocates the use of antimony tri- and penta-chloride at 40° to 50°C., distilling the product. Dreyfus, Tompkins, and the Clayton Aniline Co. (B.P. 8438, 1909) claim the production of chlor- or brom-acetylides by passing acetylene into antimony pentachloride or pentabromide and the use of the acetylide as a catalyst in production of halogen indigos and thio-indigos. Other patents claim the production of tetrachlorethane by mixing the gases in presence of solid diluents such as sand, clay, infusorial earth, etc., subsequently passing the mixed gases into liquids such as antimony chlorides or their solution in tetrachlorethane (Chem. Fabr. Griesheim-Elektron, B.P. 13411, 1907 ; G.P. 372193, 1920). Consort. f. Elektrochem. Ind. G.m.b.H. (B.P. 25967, 1910) claim that ferric chloride is an efficient catalyst. Lidholm (B.P. 22094, 1905) recommends dilution with an inert gas. Salzbergwerk Neustassfurt suggest the use of sulphur chloride to which a small amount of iron has been added (G.P. 174068). Hofer and Mugdan (U.S.P. 985528, 1910) use ferric chloride as catalyst. Ornstein and Bloxham (B.P. 2375, 1911) use iron as catalyst.

Progress in processes for the manufacture of tetrachlorethane has been chiefly in the direction of finding safe continuous methods. Le Floch (F.P. 491200, 1919) and H. H. Dow (U.S.P. 1437636, 1922) both claim the formation of tetrachlorethane by alternate adsorption of chlorine and acetylene by active charcoal. Maze (U.S.P. 1425669, 1922) passes acetylene into caustic alkali saturated with chlorine.

Comp. Prod. Chim. d'Alais et de la Camargue (B.P. 132757, 1919) pass the two gases through iron turnings mixed with broken quartz, sprinkling the solids continuously with tetrachlorethane. The flow of liquor serves to control the temperature of the reaction.

Holzverkohlungs Ind. A.-G. (G.P. 387452, 1921) describes a preparation by passing the two gases over $CaCl_2$, $FeCl_3$, or $CuCl_2$ at 500°, the gases being diluted with steam. Tako (U.S.P. 1812542) passes C_2H_2 and Cl_2 over iron filings mixed with an adsorptive substance, such as bone charcoal. Sadago Igi (J. Chem. Ind. Japan, 1920, **23**, 1217) states that the optimum temperature for the adsorption of the chlorine is 80°–100°C., and for the acetylene 60°–80°C. $SbCl_5$ is the catalyst, and the reaction is stated to depend on the intermediate formation of $SbCl_3$. Miloslavski and Postovski (J. Chem. Ind. Russ. 1930, **7**, 141) describe experiments on the direct union of C_2H_2 and Cl_2; they base their apparatus on that described in G.P. 204883, 1906, and 368892, 1919 (Chem.

Fabrik Griesheim-Elektron); it consists of a tube packed at the top with inert material to mix the two gases, the catalyst being in the lower portion from which the liquid formed drips out. Experiments were carried out at first with clean sand as a catalyst, and later with sand mixed with iron. Gas rates up to 0·65 litre per min. of C_2H_2 and a gas ratio of $1C_2H_2 : 2Cl_2$ gave no explosion in the tube, but increasingly violent explosions occurred with increasing velocities. The reaction takes place so slowly with an inert contact material that the process would be useless. At higher velocities the reaction $C_2H_2+Cl_2=2HCl+2C$ causes great heat evolution and explosions, and for the action to be safe and economic a catalyst is necessary. With a constant gas speed the optimum results were obtained with 30% iron and 70% sand as catalyst, and the rise to the optimum temperature was rapid. With 5% iron the conversion fell to 15%. Temperatures are best kept between 70° and 200°, the higher the temperature the less pure is the product. The chief criteria for the catalyst are large contact surface and low thermal conductivity. Catalysts consisting of sand with iron, iron oxide and natural iron ores were tried, and in some cases were better than the sand and iron mixture, higher gas speeds being permissible. Sand and alumina was unsatisfactory, explosions occurring. The effect of impurities, *e.g.* H_2S and PH_3, in the acetylene neither slowed down the reaction nor decreased the yield. Kraft and Alexeev (J. Chem. Ind. Russ. 1931, **8**, 861) state that tetrachlorethane was obtained without explosion by passing C_2H_2 and Cl_2 up a tower packed with Fe_2O_3 granules, down which tetrachlorethane containing 0·01% $SbCl_5$ flowed at 30°C. In Polish P. 20000 (Chem. Zentr. 1935, **106** [ii], 2580) a process for synthesis of tetrachlorethane by passing chlorine and acetylene through a wire gauze catalyst is described. The preparation from dilute C_2H_2 by passage with Cl_2 over a catalyst consisting of iron, iron compounds, or silica gel is described in B.P. 413632 and G.P. 613607, Ruhrchemie A.-G.

The uses of tetrachlorethane depend on its solvent properties, but its use has decreased very considerably recently owing to its toxic nature, trichlorethylene and perchlorethylene having taken its place. It was used during the first year of the War in an aeroplane dope, but this was discontinued in 1915 owing to the toxic properties of its vapour. It is also an excellent sulphur solvent, the two being completely miscible above the melting-point of sulphur. Towards metals tetrachlorethane is said to be indifferent if dry, but in the presence of a trace of water it attacks Fe, Zn, and Al. Tetrachlorethane and pentachlorethane are the worst of these solvents in this respect. Crudes (Ind. Quim. 1916, **18**, 265) states that tetrachlorethane, even when dry, attacks Al, and in presence of moisture when heated causes deep-seated decomposition. The rate of attack on metals is somewhat reduced in the presence of oil seeds. The rate of corrosion of cast iron, Cu, and Pb is sufficiently slow to permit of their use for plant for manufacture and distillation. The action of chlorinated ethylenes and ethanes on the alkali metals has been studied by Staudinger (Z. angew. Chem. 1922, **35**, 657 ; G.P. 396209, 1924) and extended by Lenze and Metz (Z. ges. Schiess- u. Sprengstoffw. 1932, **27**, 255, 293, 337, 373) with a view to possible use in explosives. Tetrachlorethane reacts explosively with K but not with Na. Towards alkalis tetrachlorethane is very unstable, losing HCl to form trichlorethylene even with mild alkalis. Heated at 300°C. it decomposes to form HCl and trichlorethylene, which with further heating gives perchlorbenzene. It is stable to acids and mixes in all proportions with HNO_3 ; the solution is, however, precipitated by water. With fuming H_2SO_4 in presence of copper or mercury salts it is converted to glyoxal sulphate, which, on heating with water, forms glyoxal (G.P. 362743, 1919, Chem. Fabrik vorm. Weiler ter Meer, Uerdingen am Rh.). Müller and Lubor (Ber. 1932, **65** [B], 985) have investigated the action of ultra-violet rays on tetrachlorethane and state that in moist air the following products are formed, hydrochloric, oxalic and dichloracetic acids and octochlorbutane, and in dry air hydrochloric acid and dichloracetyl chloride. With chlorine in sunlight, or in presence of $AlCl_3$, it is further chlorinated to pentachlorethane and hexachlorethane. It has been proposed as an insecticide for vine louse (Grether, G.P. 283311, 1921), and is used to a considerable extent for the extermination of white fly in tomato. It still finds a use in textile soaps, but where possible it should be replaced by trichlorethylene or perchlorethylene.

Trichlorethylene. *Preparation.*—Methods of preparation may be divided into two sections :

(*a*) from tetrachlorethane by treatment with alkalis ;

(*b*) from tetrachlorethane by thermal decomposition with or without a catalyst.

(*a*) Trichlorethylene is made with quantitative yield from tetrachlorethane by heating in a still with milk of lime or dilute alkalis (Consort. f. Elektrochem. Ind. G.m.b.H., G.P. 171900, 1905). The use of solid lime is described by the same firm in G.P. 208854, 1907, who claim that dry calcium chloride and trichlorethylene can be obtained. Sadago Igi (J. Chem. Ind. Japan, 1920, **23**, 1217) states that lime and water should be in excess, and that an 84% yield is easily obtained. Miloslavski and Postovski (J. Chem. Ind. Russ. 1930, **7**, 1414) state that the theoretical quantity of CaO and double the theoretical quantity of water are necessary. Tompkins (B.P. 19568, 1904) describes the preparation by passing NH_3 into tetrachlorethane and alcohol. Ammonia is also recommended by Comp. des Prod. Chimique d'Alais et de la Camargue (G.P. 351463, 1921). The same firm in B.P. 132755, 1919, describes its preparation by heating tetrachlorethane with aqueous NH_3 in an autoclave at 140°–170°C., or by passing NH_3 into tetrachlorethane and water at 70°C. Guyot (U.S.P. 1343716, 1920) recommends aqueous ammonia at 60°C.

(*b*) Several methods of conversion of tetrachlorethane to trichlorethylene by thermal decomposition are described in the patent literature, but it is not known to what extent this method is worked commercially. Tompkins and Clayton Aniline Co. (B.P. 23780, 1906) state that it is formed by passing tetrachlorethane through a tube at 400°–500°C. Some hexachlorbenzene is formed at the same time. Chem. Fabrik Griesheim-Elektron (G.P. 263457) describe its formation by passage over bi-valent metallic chlorides, specifying $BaCl_2$ and $CaCl_2$, but a good product is not easily obtained. Chem. Fabirk Buckau (G.P. 274782, 1912) claim the preparation by passage over ThO_2 at a temperature not exceeding 390°C. Soc. Bozel Maletra (F.P. 715421) pass tetrachlorethane over pumice impregnated with copper phosphate, and Consort. f. Elektrochem. Ind. G.m.b.H. (B.P. 302321, 1927) pass tetrachlorethane over large surfaces at very high speed, and specify as contact materials wood charcoal, active carbon, pumice, silica gels, metal oxides, or salts. Yamaguchi (J. Chem. Soc. Japan, 1934, **55**, 1227, 1232) states that the dechlorination of $C_2H_2Cl_4$ by charcoal is not effective at 250°–300°C. and the yield decreases with increase of temperature. Addition of NH_4OH accelerates and of $C_2H_5{\cdot}OH$ retards the reaction, which is of the second order.

Physical properties (*see* Table I).—Other physical properties of importance are absolute viscosities (C.G.S.), which are 0·005490 at 25°C., 0·004466 at 50°C., 0·003709 at 75°C. The specific volume is 0·6878 at 25°C., 0·7078 at 50°C., 0·7288 at 75°C. (Herz, Z. Elektrochem. 1917, **23**, 24). The vapour pressures at various temperatures are (Herz and Rathmann, Chem.-Ztg. 1912, **36**, 1417) :

25°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.
73	94	149	224	324·5	453	618 mm. Hg

Heat conductivity is 0·000257 grm. cals./sec./sq. cm./°C./cm. at 18°C., and 0·000296 at 30°C.

The solubility of water in trichlorethylene is given as :

−30°C.	−20°C.	−8°C.	0°C.
0·0025	0·0050	0·0075	0·0100

6°C.	10°C.	20°C.	25°C.
0·0125	0·0170	0·0250	0·0325%

(Carlisle and Levine, Ind. Eng. Chem. 1932, **24**, 1165).

Azeotropic mixtures are formed between trichlorethylene (A) and several other solvents, and some of these are shown in Table II.

TABLE II.

Solvent B	Solvent C	Molecular % A	Molecular % B	Molecular % C	B.p. °C. at 760 mm. Hg.
Methyl alcohol	—	30	70	—	60·2
Ethyl ,,	Water	38·4	41·2	20·4	67·25
n-Propyl ,,	—	69	31	—	81·75
,, ,,	Water	51·1	16·6	32·3	71·55
iso-Propyl ,,	—	54	46	—	74
iso-Butyl ,,	—	86	14	—	85·4
tert-Butyl ,,	—	74	26	—	75
Allyl ,,	—	70	30	—	80·95
,, ,,	Water	49·2	17·3	33·5	71·4
tert-Amyl ,,	—	83	17	—	—

For partition coefficients of I_2, $C_6H_5{\cdot}OH$, and $(CH_3)_2CO$ between trichlorethylene and water, *see* Herz and Rathmann (Z. Elektrochem. 1913, **19**, 552).

Chemical properties. — Trichlorethylene is quite stable towards dilute alkalis and dilute acids. With hot strong alkalis it gives the salt of glycollic acid, which, in turn, reacts to form dichloracetylene, C_2Cl_2. Consort. f. Elektrochem. Ind. G.m.b.H. own a patent (G.P. 257878, 1912) for making glycollic acid salts by heating trichlorethylene with $NaOH$ or $Ca(OH)_2$ in an autoclave at 150°C. A good yield is claimed. With sodium ethoxide it forms dichlorvinyl ether, which hydrolyses to monochloracetic ester :

$$C_2HCl_3 + NaOC_2H_5 = NaCl + C_2HCl_2{\cdot}OC_2H_5$$

$$C_2HCl_2{\cdot}OC_2H_5 + H_2O = HCl + CH_2Cl{\cdot}CO_2C_2H_5$$

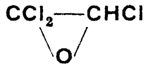
(Imbert and Consort. f. Elektrochem. Ind. G.m.b.H., G.P. 216940, 209268 (1906), 194884 (1907)). It is unlikely that this process can compete with manufacture from acetic acid. The action of KOH was investigated by Ott, Ottmeyer, and Packendorff (Ber. 1930, **63** [B], 1941 ; 1931, **64** [B], 1324), who state that provided the temperature is not allowed to exceed 130°C., and that no local heating occurs, trichlorethylene will react smoothly with solid KOH dried at 200°C. The smooth reaction depends on the presence of 1% of silicate, and in its absence the reaction is explosive. It reacts explosively with potassium and violently with barium (Lenze and Metz, *l.c.*). Trichlorethylene reacts with concentrated sulphuric acid to give monochloracetic acid, in which preparation the mixture must be heated, and water continuously added in order to keep the acid concentration constant at about 90%. The yield should be 90–100% of the theoretical. Continuous separation of the product is described. Aryl and alkyl sulphonic acids may be used in place of sulphuric acid to give the corresponding products. The method is of little practical value to-day owing to competition of direct synthesis from acetic acid (*see* Simon and Chavanne, U.S.P. 1304108, J.S.C.I. 1919, **35**, 553A ; Compt. rend. 1923, **176**, **309** ; Comp. Prod. Chimiques d'Alais et de la Camargue, G.P. 359910, 383029 (1920), 377254 (1922) ; Austral. P. 89199 (1920), 89200 (1922), F.P. 541669 (1923)). For use of alkyl and aryl sulphonic acids, *see* G.P. 377411, F.P. 519813 (1918), 20064 (1920), Swiss P. 97056 (1921). With H_2SO_4 and paraformaldehyde it yields the ether of chlorhydracrylic acid,

$$O[CH_2{\cdot}CHCl{\cdot}COOH]_2$$

Prins (Rec. trav. chim. 1932, **51**, 469). With fuming nitric acid the reaction is uncontrollably violent, but when refluxed with concentrated nitric acid it gives dichlordinitromethane, which can also be obtained by treating an aqueous solution of potassium chlorodinitromethane with chlorine (Burrows and Hunter, J.C.S. 1932, 1358). Trichlorethylene is converted to pentachlorethane by addition of chlorine in presence of a catalyst, but **is** inert to iodine and to iodine solutions **which** have ICl as their active agent. It can therefore be used in place of CCl_4 with Hübl or Wijs solutions (Margoshes and Baru, J. pr. Chem. 1921, **103**, 216). With aluminium chloride on boiling for 15 hours it is stated to give the pentachlorobutadiene, $CHCl : CCl{\cdot}CCl : CCl_2$, b.p. 85°–91°C., 20 mm. With HCl gas and $AlCl_3$ at 50° it is said to form pentachlorobutadienes and hexachlorbenzene (Müller and Hönn, J. pr. Chem. 1932 [ii], **133**, 289). With Cl_2O it is converted to chloral, $CCl_3{\cdot}CHO$, and *octa*chlorodiethyl ether,

$$(CCl_3{\cdot}CHCl)_2O$$

(Goldschmidt and Schüssler, Ber. 1925, **58** [B], 566). On oxidation it is said to yield equal parts of dichloracetyl chloride and a new compound, probably



which can be converted to $CHCl_2{\cdot}COCl$ or $CCl_3{\cdot}CHO$ (Consort. f. Elektrochem. Ind. G.m.b.H., B.P. 363099). For a discussion of the mechanism of the oxidation of trichlorethylene, *see* Erdmann (J. pr. Chem. 1912, **85** [ii], 78); Staudinger (*ibid.* 1912, **85** [ii], 330).

The reaction with milk of lime and aniline to form phenyl glycine is interesting. An aqueous suspension of trichlorethylene, or tetrachlorethane, is heated with milk of lime and aniline to 140°–190°; alkali hydrates, carbonates, aluminates, silicates, and zincates may be used in place of lime. The reaction takes place with the intermediate formation of Sabanejev's base (Annalen, 1875, **178**, 125), which hydrolyses successively to phenyl glycine anilide and phenyl glycine.

The process can be carried out continuously (Imbert, Levinstein, and British Dyestuffs Corporation, B.P. 173540; Wyler and British Dyestuffs Corporation, B.P. 188933; British Dyestuffs Corporation, G.P. 436620, 437409).

The reaction between trichlorethylene, and aniline in the presence of alkali has been more closely investigated by Ruggli and Marslak (Helv. Chim. Acta, 1928, **11**, 180), who show that Sabanejev's base is phenylglycinediphenylamidine, $NHPh{\cdot}CH_2{\cdot}C(: NPh){\cdot}NHPh$, m.p. 189°–190°, and obtained similar condensation products from trichlorethylene with *p*-toluidine, *p*-anisidine, *p*-phenetidine, and 4-aminodiphenyl.

The influence of trichlorethylene on the combustion and explosive limits of combustible gas mixtures is of interest. 10% of trichlorethylene reduces both the lower and higher limits of explosion of methane-air mixtures from 5·24 and 14% to 3 and 7·5% respectively, according to Coward and Jones (Ind. Eng. Chem. 1926, **18**, 970). Similar results are given by Jorissen and Meuwissen (Rec. trav. chim. 1925, **44**, 132), who attribute the lowering of the limits to the decomposition of trichlorethylene at the flame temperature followed by combustion of the products (*see also* Jorissen and Langen van der Valk and Jorissen and Velíšek, Rec. trav. chim. 1925, **44**, 810; 1924, **43**, 80). The effect on carbonic oxide and air mixtures is to lower the limits and to decrease the explosive range; 4% trichlorethylene prevents explosion (Langen van der Valk, Rec. trav. chim. 1929, **48**, 201). Trichlorethylene is not itself normally inflammable, but it is possible to cause the vapour to explode when mixed with the right quantity of air between 65° and 77°C. It has a marked influence on the flash-points of inflammable materials. A white spirit (boiling range 153°–205°C.) flashing at 44°C. showed no flash-point at 95°C. when mixed with 40% of its weight of trichlorethylene; and kerosene (boiling range 164°–284°C.), flashing at 66°C., did not flash at 95°C. with 20% of trichlorethylene. Similar reductions can be obtained with acetone, benzene, etc., but it should be remembered in using mixtures that fractional evaporation may occur and alter the composition of the liquid and vapour.

Stability of trichlorethylene.—The stability of trichlorethylene is intimately connected with its corrosive action on metals and, as such, is of great importance in industrial applications, but there is little literature available on this subject. Sadago Igi (J. Chem. Ind. Japan, 1920, **23**, 1217) states that while wet tetrachlorethane corrodes iron, wet trichlorethylene does not. Drozdov (J. Chem. Ind. Russ. 1934, **2**, 53) states that water promotes corrosion; Formánek (Chem. Obzor. 1930, **5**, 57), comparing carbon tetrachloride, trichlorethylene, and tetrachlorethane, states that the effect of trichlorethylene on Cu, Brass, Sn, and Fe covered with Fe_3O_4 during 8 weeks is very small; Crudes (Ind. Quim. 1916, **13**, 265) gives a report of the effect of steel, Cu, Ni, Al, and Pb on various chlorinated solvents, and states that they are liable to decompose when impure; but these papers do not give details or reliable figures. Carlisle and Levine (Ind. Eng. Chem. 1932, **24**, 1165) give figures for stability and corrosion tests; in tests extending over one year, factory grade pure trichlorethylene did not show the development of any acidity when stored in metal drums or in glass-stoppered bottles in the dark; they state that decomposition on exposure to sunlight depends on the presence of oxygen, acidity developing in its presence, but not in its absence. The influence of metals is negligible on the development of acidity either in dry or moist trichlorethylene. The vapour is said not to be decomposed by heating up to 200°C., but above that temperature some decomposition occurs. The effect of water is not noticeable. It is stated that, heated in presence of oxygen, some acidity is developed, but this is prevented by use of a stabiliser. The corrosion of mild steel, Sn, Brass, Cu, Pb, and Al was measured, though the tests only extended over a period of 24 hours. With unstabilised trichlorethylene, slight corrosion occurred with all the metals, but in trichlorethylene containing a stabiliser the corrosion, even in the presence of water, was negligible beyond the formation of a dull film on mild steel. Gowing-Scopes (Analyst, 1914, **39**, 4) investigates the corrosion of many metals by a range of chlorinated solvents, but does not include figures for extent of corrosion. In commercial practice it is customary to add some stabiliser to trichlorethylene, and the patent literature contains numerous references to these additions. The recommended stabilisers range from hydrocarbons of both the paraffin and benzene series ; hydroxy compounds such as phenol and hydroquinone ; coumarin to alkaline materials such as alkylamines, which not only stabilise the trichlorethylene but also neutralise any acid which might be formed. The amount of stabiliser usually added is 1% or less, and is insufficient to have any appreciable effect on the physical properties of the liquid. (*See*, for example, Consort. f. Elektrochem. Ind. G.m.b.H., F.P. 726362; Dangelmajer, Canad. P. 303663; Roessler and Hasslacher, Chem. Co., F.P. 732569; Du Pont de Nemours, U.S.P. 1996717 ; Canadian Industries, Ltd., Canad. P. 341792.) Some light has been thrown on the stability of trichlorethylene by the discovery of the formation of certain chloro-butane derivatives in crude tetrachlorethane which decompose spontaneously during the conversion process, yielding hydrogen chloride. Possibly some of the corrosive effects may originate in these impurities (Müller and Hüther, Ber. 1931, **64** [B], 589). To summarise the corrosive properties of trichlorethylene, moist trichlorethylene exposed to sunlight develops acidity and is corrosive. The corrosion of metals by stabilised trichlorethylene in the dark, or in metal containers, is negligible, and apparatus for its use can be made of copper, brass, or steel, preferably galvanised. Steel which has been cleaned by trichlorethylene tends to rust owing to the removal and absence of any protective grease film, and galvanising is therefore desirable for plant which is alternately exposed to the action of trichlorethylene and air

Uses of trichlorethylene.—The applications of trichlorethylene depend almost entirely on its solvent properties and it has a wide application in many industries for solution and extraction of oil. Advantages which are claimed for its use are the ready solubility of most oils, fats, and waxes, the rapid penetration into material owing to low surface tension and viscosity, its stability and non-corrosive properties, its low boiling-point and low latent heat, and the ease with which it is recovered, leaving an uncontaminated product, and also its non-inflammability and relatively low toxicity.

Solubility of materials in trichlorethylene.—Webster and Bruins (Pharm. Weekblad, 1914, **51**, 51) summarise the solubilities of many substances. Ordinary acids, glycosides, sugars, alkaloid salts, tannins and theobromines are practically insoluble. Benzoic acid, free alkaloids, anthracene, coumarin, sulphur are fairly soluble ; resins and fats usually dissolve easily. It is upon these relative solubilities that many extractions with trichlorethylene depend. The following are some solubilities in grms./100 grms. given by these workers (*see* original for others) :

Brucine	2·56
Codeine	12·0
Camphor	14·0
Caffeine	0·76
Glucose	0·006
Nicotine	6·5
Piperine	9·83
Sulphur	1·16
Tannin	0·012
Theobromine	0·008

The solubility of paraffin waxes was studied at various temperatures and with varying amounts of oil in the trichlorethylene with reference to the solvent dewaxing of oils (Poole and others, Ind. Eng. Chem. 1929, **21**, 1098 ; 1931, **23**, 170 ; 1932, **24**, 1215). Buchner (Chem.-Ztg. 1928, **52**, 319) states that beeswax is 30% soluble at ordinary temperatures. Stearic acid, paraffin, tallow and pitch are completely soluble ; and carnuba and ceresin waxes and ozokerite are difficultly soluble. Gowing-Scopes (Analyst, 1914, **39**, 4) gives the approximate solubilities of 248 different organic compounds.

Metal cleaning.—The most common use of trichlorethylene is for cleaning metal surfaces which have grease on them, either to remove grease from the surface because its presence is objectionable, or because its presence prevents proper subsequent treatment of the material, *e.g.* prior to electro-plating, galvanising, Parkerising, printing, etc. Metal cleaning can be divided into two sections, vapour degreasing and liquor degreasing. In the former, trichlorethylene is boiled in a tank and the article to be cleaned is immersed in the vapour, when trichlorethylene condenses on the surface of the cold metal, cleaning it with a constantly renewed supply of clean solvent. The condensation continues until the article has reached the boiling-point of trichlorethylene, when it is usually quite clean and can be removed from the apparatus. Owing to the low surface tension, very little liquor remains on the article, and this is quickly evaporated by the heat content of the metal, leaving it clean and quite dry. The degreasing time is from a few seconds to 3 or 4 minutes, according to the amount of metal undergoing treatment. The limitation of this method is determined by the heat capacity of the article to be cleaned, which, if it is too small, will not condense sufficient vapour to dissolve all the grease. In this case a liquor wash is necessary and plants can be designed on these lines, or on a combination of liquor and vapour treatments. Plants are sold based on these two treatments for a variety of purposes, both for continuous and discontinuous working. The detailed design of plants is very important, as on this depends the solvent loss, which is made up of loss due to diffusion from the apparatus, together with loss of liquor carried off on the cleaned articles. Descriptions of degreasers may be found in Jesson, Metallurgia, 1932, **7**, 37 ; Krause, Mitt. Forschungsinst. Probieramt Edelmet, 1932, **6**, 13 ; Wallace, Chem. Zentr. 1932, **103** (1), 2232 ; Halls, Chem. Age, 1932, **26**, 372 ; Wernick, Ind. Chem. 1934, **10**, 479 ; also in the patent literature.

Wool degreasing.—The removal of grease and oil from raw wool by cleaning with trichlorethylene gives good fibre cleaning and avoids the fire hazard. It assists in giving good felting properties. It is claimed also that an increased yield of wool is obtained (Chem. Trade J. 1934, **95**, 292). Coghlan (B.P. 170645, 1921) describes a plant in which the wool is placed in a wire cage suspended in an extraction tank. Four of these tanks are connected in one circuit, and trichlorethylene flows through them in series. The trichlorethylene and extracted grease are separated by distillation. The degreased wool is removed from the first tank, and fresh wool added. The cycle is then repeated but starting with the second tank. Trichlorethylene remaining in the wool is recovered by treatment with warm water or hot carbon dioxide which passes to a separator or condenser. In another type of plant (German) the wool is placed in a vessel filled with solvent, which is then siphoned out, carrying the grease in solution, and the extraction vessel is refilled from an overhead vessel. The solvent is distilled, leaving the grease behind, the condensed solvent flowing to the overhead feed tank. The process is repeated as often as required to clean the wool, and the residual trichlorethylene is removed from the wool by heating the chamber with a steam coil (Drake, Chem. Zentr. 1933, **104**, I, 695, 699 ; 1932, **103**, I, 760 ; Hey, J. Bradford Textile Soc. 1919–20, 39 ; Textile Mercury, 1935, **92**, 265 ; Chem. Zentr. 1935, I, **106**, 3738).

Leather degreasing.—Trichlorethylene is used to some extent in leather degreasing, more particularly on the Continent, to remove the excess fat from the hides, particularly in light shades. Recovery of oil from bones and leather scrap by extraction with trichlorethylene is practicable. Bela Lach (Seifensied.-Ztg. 1919, **38**, 394, 421) discusses its advantages as a solvent for bone degreasing. *See also* Stang (Landw. Versuchs-Stat. 1926, **105**, 43).

Seed extraction.—Seed extraction may be carried out with two objects, to recover an edible oil, or to recover an oil-free seed. These extractions are usually similar to the wool degreasing process, using three or more washes of liquor on the seeds in an extraction chamber, and distilling the solvent from the liquor in a still. Olive oil is extracted in this way, avoiding the use of inflammable carbon bisulphide or benzene, and less than 1% oil can be left in the olive rind. In the vegetable oil industry the most powerful presses leave 8–10% of oil in the press cake. Cracklings hold 12–25% ; hair, tankage and glue-kettle residues hold 11–14%. This fat can be very favourably extracted by trichlorethylene. It may also be used for nuts, castor beans, press cake, soya beans, flax seeds, etc. *See* Seivers and McIntyre, Chem. & Met. Eng. 1922, **26**, 603 (for mixed solvents) ; Tänfel and Standigel, Allgem. Oel- Fett-Ztg. 1930, **27**, 129, 148 (flax seeds) ; Stang (*l.c.*) ; Bennett, Oil and Colour Trade J. **64**, 829 (olive husk extraction plant), F.P. 701960 (1932). Caffeine extraction from coffee beans to give caffeine and coffee free from the alkaloid is very similar. The last traces of trichlorethylene are removed by heating the coffee.

Dry cleaning.—By reason of its non-inflammability and non-explosive nature, trichlorethylene is rapidly growing in favour for dry cleaning, particularly in small plants where it is not convenient to take elaborate anti-fire precautions. The absence of corrosive effects allows common metals to be used for construction of dry-cleaning equipment. It is claimed that pre-spotting is unnecessary as stains are not set and they can usually be removed by water afterwards. A better feel and finish is obtained and materials do not become harsh. The tensile strengths of natural and artificial fabrics are unaltered by trichlorethylene and shrinking is avoided. Only a few minutes' freshening period after drying is necessary, and no after-smells are noticeable, which is a distinct advantage. The whole operation will normally take about 20 minutes for washing and centrifuging, and 20–30 minutes for drying. It is customary to use special soaps for dry cleaning when they are considered necessary, and these usually consist of partially saponified fatty acids, the excess acid serving to keep the soap in solution (*see* Brown, Dyer and Calico Printer, 1932, 414 ; Brown, Dyer, 1932, 79 ; Brown, Chem. Markets, 1932, 25 ; Power Laundry, 1933, 201 ; 1935, **51**, 53 ; Bird, J. Soc. Dyers and Col. 1933, **49**, 379 ; 1934, **50**, 72 ; Chem. Age, 1934, **31**, 1460).

Dewaxing of oils.—A process which has attracted some attention on the Continent is the removal of wax from oils by trichlorethylene, and known as the de Laval S-N process. It depends on the relative solubilities of oils and wax at high and low temperatures. It is claimed that trichlorethylene gives better separation than benzene, with much shorter working times, owing to increased cooling rates. The non-inflammability is a great advantage (Chem. Age, 1932, **27**, 575). A description of the Standard Oil Company's plant is given in Petrol Times, 1934, 222.

Dehydration of alcohols.—Fritzweiler and Dietrich (Z. angew. Chem. 1932, **45**, 605 ; 1933, **46**, 241) outline a modern process for dehydration of alcohol by azeotropic distillation in the presence of trichlorethylene, stating that compared with benzene it has a higher " dehydrating power " and also advantages in heat consumption (*cf.* Analyst, 1913, **38**, 424). A similar use is in the separation of formic and acetic acids depending on the distillation of the mixed acids with trichlorethylene ; at 75°–80°C. the condensate separates into two layers, the upper layer being an azeotropic mixture of formic acid and trichlorethylene and the lower trichlorethylene alone (I.G. Farbenind. A.-G., B.P. 305594).

Uses in analysis.—Trichlorethylene can be used satisfactorily for analysis of fats in various foodstuffs. Methods have been devised for analysis of meat, milk, chocolate, and various meals and cakes (Grossfield, Chem.-Ztg. 1925 (2), **49**, 1499 ; 1927, **51**, 617 (fats) ; Hyatt, J. Sci. Tech. New Zealand, 1930, **11**, 418 (bituminous material) ; Gowing-Scopes, Analyst, 1914, **39**, 4).

Insecticidal and germicidal properties.—Trichlorethylene has marked germicidal properties, and several papers are to be found on its action as a fumigant for seeds. Hoyt (Ind. Eng. Chem. 1928, **20**, 835) found 100% kill of all insects at 7 lb./100 cu. ft. with no effect on the seed germination. Muller (Chem.-Ztg. 1927, **51**, 510) discusses its effect on barley seeds. Young (J. Agric. Res. 1929, **39**, 925) recommends it for killing lice weevils in cereals. For uses in emulsified form as a disinfectant, *see* Rimpan (Z. Hyg. 1931, **112**, 208). Joachimoglu (Biochem. Z. 1921, **124**, 130) states that the molecular percentage for lethal results on *Vibrio Metschnikoff* is 0·005372.

Textile soaps.—Trichlorethylene is often incorporated in water-soluble textile soaps which emulsify in water and are sold under various trade names. They have a remarkable power for removing grease in laundry work. It is usually emulsified in sulphonated oils, or with fatty acid soaps and alcohols, *e.g.* Deckert (Seifensied.-Ztg. 1925, **52**, 975) states that a mixture of an alcoholic solution of sodium oleate (55%) and trichlorethylene containing 4·72% of the soap gives permanent emulsions for textile work.

Trichlorethylene also finds uses as a paint thinner, rubber cement, solvent in paint remover, in various polishes, and has an increasing use for removal of machine-oil and dirt from textiles which contain oil and dirt when removed from the loom. A recent use is as a cooling bath with solid CO_2 for shrink fitting (Imperial Chemical Industries, B.P. 423105).

Dichlorethylene, CHCl : CHCl.—Dichlorethylene is usually made by heating tetrachlorethane with iron turnings and distilling the product to remove tetrachlorethane. It can be made from acetylene and chlorine directly. Acetylene is said to react with tetrachlorethane to give dichlorethylene when passed over suitable catalysts, particularly hydrogenation catalysts such as Ni, nickel compounds or active carbon. Trichlorethylene is made as a by-product (Chem. Fabr. von Heyden A.-G., G.P. 566034). For properties, *see* Table I. Some confusion exists as to the relation of the two isomers, some authors describing the higher boiling material as the *cis* form, others the lower. The latter convention has been adopted in International Critical Tables, the former in Ullmann's Enzykl. techn. Chem. and here. Chavanne (Bull. Soc. chim. Belg. 1914, **28**, 234) measured the rate of addition of bromine to the two isomers, and work on the same subject was carried out by Verhoogen (*ibid.* 1926, **34**, 434) which showed that the higher boiling liquid had the *cis* form. It can now be obtained commercially as the ordinary equilibrium mixture with a boiling range of 48°–65°C., or in pure *cis* and *trans* form for special purposes. The *trans* form with its low boiling-point has some uses as a substitute for ether in extraction work as it is much safer. The hot vapour of dichlorethylene is inflammable but burns with a cold, easily extinguished flame. If vapour above the cold liquor be ignited, the heat of combustion will usually not evaporate the liquor fast enough to support the fire. Its chief use is as a rubber solvent, for paint removers, and special fat extractions where a lower temperature is required than can be obtained with trichlorethylene. Its use as a refrigerant (*trans* form) has been patented (Carrier Engineering Co., Ltd., B.P. 238263). With fuming sulphuric acid it gives chloracetaldehyde sulphonic acid, which, with 80% H_2SO_4, gives chloracetyl chloride (Chem. Fabrik. vorm. Weiler t. Meer, Uerdingen am Rh., G.P. 362744, 1921).

Perchlorethylene (tetrachlorethylene), C_2Cl_4, is prepared by heating perchlorethane with milk of lime and as a by-product in the manufacture of trichlorethylene. Mailhe and Sabron (Bull. Soc. chim. 1930 [iv], **47**, 349) state that it can also be made by passage of pentachlorethane and hydrogen over nickel at 270°C. Chemically it is very similar to trichlorethylene, being very stable and can be used as a substitute for trichlorethylene where a higher boiling-point solvent is required and it is used in some dry-cleaning operations. Its chief use is in textile soap manufacture, and it has an extending use for the treatment of hook worm and liver fluke in sheep and cattle (Shulz and Dewtjan, J. Pharmaz. Ind. Russ. 1934, **3**, 44 ; Chem. Zentr. 1935, **106**, I, 2210).

With H_2SO_4 and HNO_3 it gives trichloracetyl chloride and tetrachlordinitroethane (Blitz, Ber. 1902, **35**, 1529). Boiling concentrated HNO_3 has no action, but fuming HNO_3 acts violently forming CO_2, nitrogen oxides, and HCl (Burrows and Hunter, J.C.S. 1932, 1357). With paraformaldehyde and sulphuric acid it forms 2 : 2-dichlorhydracrylic acid, which is extremely hygroscopic (Prins, Rec. trav. chim. 1932, **51**, 469). It explodes strongly with potassium (Lenze and Metz, *l.c.*), but towards most common metals it has no action when dry and very little if moist. (For other methods of preparation, *see* Faraday, Ann. Chim. Phys. 1821 [ii], **18**, 48, from hexachlorethane ; Regnault, Annalen, 1834, **33**, 321 ; Kolbe, Annalen, 1845, **54**, 147 ; Weiser and Wightman, J. Physical Chem. 1919, **23**, 415 ; Besson, Compt. rend. 1894, **118**, 1347 ; 1910, **150**, 1118, from carbon tetrachloride ; Goldschmidt, Ber. 1881, **14**, 929 ; Bourgoin, Ann. Chim. Phys. 1875 (v), **6**, 142, from hexachlorethane ; Muller, Annalen, 1890, **258**, 63 ; Böeseken, Rec. trav. chim. 1910, **29**, 104 ; 1913, **32**, 12, 129 ; 1915, **34**, 75, from chloral or pentachlorpropionylchloride ; Mouneyrat, Bull. Soc. chim. 1898 [iii], **19**, 182, from pentachlorethane ; Erdmann, J. pr. Chem. 1912 [ii], **85**, 78, from trichlorethylene; Tolloczko and King, Chem. Zentr. 1913, II, 98, from petroleum gases ; A. Wacker, G.P. 464320, from pentachlorethane ; Thurn, U.S.P. 1590265, from HCl and CO over catalyst at 230°–400°C. under 1,000–3,000 lb./sq. in.).

Pentachlorethane, C_2HCl_5, is prepared in almost quantitative yield by passing chlorine into trichlorethylene in presence of catalysts or in ultra-violet light ; after washing with water and lime to remove excess chlorine it can be steam-distilled. It is also formed by chlorination of ethyl chloride (Regnault, Annalen, 1834, **33**, 321) or ethylene chloride (Pierre, J. pr. Chem. 1846 [i], **43**, 302), and by action of phosphorus pentachloride (Paterno, Annalen, 1869, **151**, 117) or aluminium chloride upon chloral (Mouneyrat, Bull. Soc. chim. 1898 [iii], **19**, 260). It is also formed by heating trichlorethylene with ferric chloride in a sealed tube (Erdmann, J. pr. Chem. 1912 [ii], **85**, 78). In solvent properties it is somewhat similar to tetrachlorethane. It is very sensitive to alkalis, yielding perchlorethylene, C_2Cl_4 ; if mixed with tetrachlorethane it reacts explosively with potassium, but potassium and pentachlorethane alone react without explosion (Lenze and Metz, *l.c.*). In the presence of aluminium chloride it is converted by chlorine to hexachlorethane (Mouneyrat, Bull. Soc. chim. 1897 [iii], **17**, 979), while aluminium chloride alone gives perchlorethylene. When passed with hydrogen over heated nickel at 270°C. it gives trichlorethylene and at 330° over nickel chloride gives tetrachlorethane (Mailhe and Sabron, Bull. Soc. chim. 1930 [iv], **47**, 349). It reacts with trichlorethylene and aluminium chloride with the formation of heptachlorpropane (Böeseken and Prins, Chem. Zentr. 1911, I, 466). It gives a deep blue colour with cuprous chloride in ammonia solution (Doughty, J. Amer. Chem. Soc. 1919, **41**, 1131). It has little action on metals if quite dry, but in the presence of moisture is corrosive.

Hexachlorethane (perchlorethane), C_2Cl_6, is produced by exhaustive chlorination of the lower chlorinated ethane derivatives (*cf.* Faraday, Ann. Chim. Phys. 1821 [ii], **18**, 48 ; Regnault, *ibid.* **69**, 165 ; Annalen, 1840, **33**, 323 ; Hübner and Müller, Z. f. Chemie, 1870, **6**, 328; Mouneyrat, Bull. Soc. chim. 1897 [iii], **17**, 794, 797 ; 1898 [iii], **19**, 454 ; Michel, Z. angew. Chem. 1906, **19**, 1095). It is also formed on passing chloroform through a red-hot tube (Ramsay and Young, Jahresber. d. Chemie, 1886, 628). It occurs as a by-product in the production of carbon tetrachloride (V. Meyer, Ber. 1894, **27**, 3160), and is formed from carbon tetrachloride by heating to 160° with amorphous arsenic (Auger, Compt. rend. 1902, **145**, 809), or by passing through a heated tube (Kolbe, Annalen, 1845, **54**, 147).

It is formed readily by refluxing carbon tetrachloride with aluminium amalgam (Hofmann and Seiler, Ber. 1905, **38**, 3058), and is also formed by direct synthesis if an electric arc be formed in a chlorine atmosphere (*v.* Boltom, Z. Elektrochem. 1902, **8**, 169 ; 1903, **9**, 209; Lorenz, Annalen, 1888, **247**, 245 ; Z. angew. Chem. 1893, **1**, 313 ; Z. Elektrochem. 1902, **8**, 203). On a commercial scale it can be conveniently prepared by the exhaustive chlorination of acetylene tetrachloride in the presence of aluminium chloride (*cf.* Mouneyrat, *l.c.*). The Salzbergwerk Neustassfürt (D.R.P. 174068) claim the production of the hexachlor compound by leading acetylene and chlorine alternately into a heated mixture of sulphur chloride and powdered iron. The same firm also claim a process for chlorinating tetrachlorethane in the presence of an artificial source of light rich in actinic rays (B.P. 1105, 1912). The pentachlor compound is formed at the same time and may be separated by allowing the mass to crystallise and then pressing the product.

Hexachlorethane forms colourless crystals which sublime without melting and have a camphor-like odour. It is used to some extent in the explosives industry in smoke-producing bombs. Heated with alkali at 210°-221°C. it gives oxalic acid (Geuther, Annalen, 1874, **111**, 174) ; alcoholic potash at 100°C. gives ethylene, hydrogen, and oxalic acid (Berthelot, Annalen, 1860, **109**, 121). Alcoholic sodium ethoxide in ethereal solution under pressure at 140°C. yields perchlorethylene (Geuther and Brockhoff, J. pr. Chem. 1870 [ii], **1**, 251). It reacts with anhydrous ammonia under pressure to give a black product of carbon and polymerisation compounds (Stahler, Ber. 1914, **47**, 912). It acts as a primer in production of chlorides of Ca, Mg, Al, Mn, Cr, Zn, Sn, and Fe (Berger, Compt. rend. 1920, **171**, 29). Sulphur trioxide at 150°C. gives trichloroacetyl chloride and $S_2O_5Cl_2$, $COCl_2$, and SO_2 (Prudhomme, Compt. rend. 1870, **70**, 1135 ; Armstrong, J. pr. Chem. 1870 [ii], **1**, 251). On passage over reduced nickel in presence of hydrogen at 270°C. perchlorethylene and HCl are formed (Sabatier and Mailhe, Compt. rend. 1904, **138**, 409), and it is also formed by reduction with alcoholic KHS or H_2SO_4 and zinc. On heating with $SbCl_5$ above 450°C. it goes completely to carbon tetrachloride (Hartman, Ber. 1891, **24**, 1019). A mixture of dichlorethane and hexachlorethane ignites with potassium (Lenze and Metz, *l.c.*).

ANALYSIS AND DETECTION.—A method of analysis of di- and tri-chlorethylene is given by Schmalfuss and Werner (Z. anal. Chem. 1934, **97**, 314) using $Hg(CN)_2$ and KOH. Weber (Chem.-Ztg. 1933, **57**, 836) gives a table of colours formed by reaction of chlorinated ethylenes and ethanes, and also carbon tetrachloride, ethylene dichloride, methylene dichloride, and chloroform, with one of the following reagents (*a*) 2% α-naphthol in *cyclo*hexanol, (*b*) or in *cyclo*pentanol, (*c*) 2% phenolphthalein in *cyclo*hexanol, in presence of H_2SO_4 or $CH_3{\cdot}COOH$ or KOH. The colours formed with different combinations of reagents serve to distinguish the solvents.

TOXICITY OF CHLORINATED SOLVENTS.

All chlorinated solvents possess narcotic properties and exposure to a sufficiently high concentration of the vapour of any of them can lead to fatal results. Little information is available regarding the physiological effects of some of these compounds, but a considerable amount of data exists on the action of chloroform, carbon tetrachloride, trichlorethylene, and tetrachlorethane. Practically all the important observations have been made on the effects of breathing the vapours.

The types of poisoning by inhalation can be subdivided into acute and chronic poisoning, although not all of the chlorinated hydrocarbons give rise to chronic effects. The acute effects are primarily on the brain. The chronic effects are degenerations chiefly of the liver and kidneys caused by the absorption of the substances over a long period in amounts that do not produce immediate acute symptoms. These two types of poisoning will be considered separately.

Acute poisoning.—Many attempts have been made to draw up lists of the relative toxicity of these compounds based upon their acute action (Müller, 1925; Lazarew, 1929; Lehmann, 1911). There is much discrepancy between their results, but a general idea of the toxicity of the various substances can be gained. All experimenters are in agreement as to the high toxicity of tetrachlorethane.

Of the chlorinated methanes, methyl chloride and methylene chloride are of similar acute toxicity but are definitely less toxic than either chloroform or carbon tetrachloride, of which chloroform is slightly the more toxic.

The first member of the chlorinated ethanes, ethyl chloride, is the least toxic of any of the chlorinated hydrocarbons commonly found in commerce. Ethylene dichloride, on the other hand, as regards toxicity resembles chloroform and according to Sayers, Yant, Waite, and Patty (1930) can give rise to lung œdema. Ethylidene dichloride (Flüry and Zernik, 1931) is less toxic than chloroform. Little is known of the toxicity of the trichlorethanes, but they are undoubtedly compounds of a fairly high toxicity. Symmetrical tetrachlorethane is well known as being a highly toxic substance and is the most dangerous of any of the more common chlorinated hydrocarbons, whilst pentachlorethane is of a similar order of toxicity. Hexachlorethane being a solid of low vapour pressure does not come into consideration.

In the chlorinated ethylene series little is known of vinyl chloride, but according to Patty, Yant, and Waite (1930) it is of similar toxicity to ethyl chloride. Dichlorethylene has only been investigated in mixtures of the *cis* and *trans* form and may be classed with trichlorethylene. Trichlorethylene and perchlorethylene are comparable to carbon tetrachloride in their acute effects.

Chronic poisoning.—It is only in the case of the more common solvents that definite information is to hand regarding chronic poisoning.

The production of toxic jaundice by tetrachlorethane was established by Willcox (1915) and his findings have been substantiated by numerous other investigators. Many fatal cases have occurred, and from the standpoint of chronic toxicity as well as of acute toxicity tetrachlorethane is the most dangerous of the chlorinated solvents.

Cases of liver and kidney damage have also arisen from continuous exposure to carbon tetrachloride (Møller, 1933). Similar damage was found by Lamson and Wing (1926) in feeding carbon tetrachloride to dogs and this compound must be classed as one which can occasionally give rise to internal degeneration.

The chronic effects of chloroform are stated by Flüry and Zernik (1931) to be of a nervous type, but chloroform can give rise occasionally to severe liver degeneration as an after-effect of acute poisoning.

The chlorinated solvents which give rise to organ degenerations in experiments on animals must be regarded as liable to cause chronic injuries on prolonged exposure to low concentrations. Of the chlorinated methanes, methyl chloride apparently does not produce any organic degeneration, but there is some doubt as to whether methylene chloride does or does not produce slight degeneration. Chloroform and carbon tetrachloride can definitely give rise to liver and kidney injuries.

In the chlorinated ethane series ethyl chloride does not give rise to internal degenerations, but of the higher members of the series ethylene dichloride, tetrachlorethane, and pentachlorethane can all give rise to degeneration of the liver and kidneys. Information is lacking with regard to ethylidene dichloride and the trichlorethanes.

Turning now to the unsaturated chlorinated hydrocarbons, little is known of any possible degenerative action of vinyl chloride and there is some difference of opinion as to whether the dichlorethylenes produce any degeneration. The experiments of Taylor (1936) prove that trichlorethylene produces no chronic degeneration in rats, whilst Lamson, Robbins, and Ward (1929) failed to produce any chronic injuries on animals with perchlorethylene.

The use of these compounds in factories comes under the Regulations in force in chemical works which deal with dangerous gases and fumes and which require the provision of adequate ventilation, breathing apparatus, and first-aid equipment. Toxic jaundice, as sometimes occurs with tetrachlorethane, is a notifiable disease

(Flüry and Zernik, Schädliche Gase, Berlin (1931); Lamson, Robbins, and Ward, Amer. J. Hyg. 1929, **9**, 430; Lamson and Wing, J. Pharm. Exp. Ther. 1926, **29**, 191; Lazarew, Arch. exp Path. Pharm. 1929, **141**, 19; Lehmann, Arch. f Hyg. 1911, **74**, 1; Møller, J. Ind. Hyg. 1933, **15**, 418; Müller, Arch. exp. Path. Pharm. 1925, **109**, 276; Patty, Yant, and Waite, U.S. Public Health Reports, 1930, **45** (**34**), 1963; Sayers, Yant, Waite, and Patty, U.S. Public Health Reports, 1930, **45** (5), 225; Taylor, J. Ind. Hyg. 1936, **18**, (4), 175; Willcox, Lancet, 1915, 544.) S. W. R.

ACETYLENE, ITS USE IN INDUSTRY.

HISTORICAL DATA.

The gas which is at present known as Acetylene was discovered by Edmund Davy in 1836, who gave to it the name "Bicarburet of Hydrogen" (Proc. Roy. Soc. 1836, 62). Berthelot in 1860 named the gas Acetylene, assigning to it the formula C_2H_2 as the simplest member of the C_nH_{2n-2} series of hydrocarbons.

Davy first obtained acetylene by decomposing potassium carbide with water, which carbide he prepared by strongly heating a mixture of calcined tartar and carbon in an iron vessel; therefore Davy not only discovered acetylene but originated the principle of obtaining it by the interaction of a metal carbide and water.

It was subsequently found that acetylene could be prepared similarly from other carbides, such as those of calcium, sodium, lithium, barium, and strontium. The highest yield of gas per unit weight is obtainable from lithium carbide.

Hare (1840) was the first to obtain acetylene from calcium carbide, and produced calcium carbide by means of an electric arc from a mixture of mercuric cyanide and lime.

Berthelot (1860) obtained acetylene by passing the vapours of alcohol, ether, aldehyde, methyl-alcohol, methane and styrolene through red-hot tubes. Wöhler (1862) produced acetylene by the action of water on calcium carbide, which carbide he obtained by intensively heating carbon in the presence of calcium and an alloy of zinc, the zinc being lost in the process of heating. Many other methods were devised or discovered for producing acetylene but no means of producing it in quantities sufficiently large to be of commercial utility. Although at the time of its discovery Davy saw and forecast its suitability as an illuminant, it found no commercial application until after 1892, when Thomas L. Willson, of Spray, in attempting to produce metallic calcium in an electric arc furnace accidentally discovered a convenient process for making substantially pure calcium carbide on a commercial scale. About the same time Moissan similarly produced calcium carbide on a small laboratory scale from lime and carbon in an electric arc furnace.

The first electric furnace for making commercial calcium carbide in Europe was erected in Leeds in 1895, and it is from this date that commercial applications began to develop.

Although electric furnaces for manufacturing calcium carbide commercially have been modified and considerably enlarged, the basic principle of manufacture and the chemical reactions of the process are still the same as those employed by Willson (*see* CALCIUM.—*Calcium Carbide Manufacture*).

With the increase in demand for acetylene during recent years, much research has been devoted to attempts to develop commercially methods for obtaining acetylene from industrial by-products such as oil vapours, methane and other hydrocarbons, with a view to utilising such waste products where they occur as surplus from other processes or in such quantities as to be an inconvenience or a hazard.

The basic principles for the conversion of such waste products to acetylene are not novel, but the mass of inventions as indicated by published patent specifications show that the problems met with in such probable development consist chiefly in (*a*) increasing the yield of acetylene, which is as yet such a small percentage of the total gases or vapours treated as to make the commercial applicability of the process doubtful, and (*b*) the difficult operations involved in effectively separating the acetylene, when produced, from the by-products and the unconverted portion of the gas or vapour.

Up to the present no source of supply for acetylene which compares favourably in cost or convenience with calcium carbide has been discovered. So far it remains the only source from which substantially pure acetylene may be obtained in either large or small quantities as required at the point of use and with comparatively inexpensive plant.

It is estimated that the annual world production of calcium carbide at the present time is of the order of 1,500,000 tons.

PRODUCTION OF ACETYLENE FROM CALCIUM CARBIDE.

Pure calcium carbide, CaC_2, which is a white semi-transparent crystalline solid, is not manufactured commercially because of its cost and the fact that it is unnecessary for the production of substantially pure acetylene. Commercial grades of calcium carbide contain only 80–85% of pure carbide. The colour ranges from dark grey to blue-black and is due to impurities occurring in the raw materials used in manufacture. The specific gravity varies from approximately 2·2 to 2·26. For commercial use it is supplied in graded sizes within specified limits according to the definite dimensions of the screens through which the pieces pass for grading after the original cast ingot has been crushed and broken.

The volume which the graded sizes occupy when packed into containers or into the gas-generating apparatus varies from 0·8–1·0 litres per kilo.

Commercial qualities are always contaminated with impurities such as iron, ferro-silicon and compounds of sulphur, phosphorus, nitrogen, etc., as well as small proportions of the uncombined raw materials lime and carbon.

Commercially, calcium carbide is sold to a standard of quality which embraces sizes of grading, proportion of dust, gas yield, and percentage of certain scheduled impurities (*see* B.S.I. Specification, Calcium Carbide, No. 642, 1935).

The chemical reaction for the generation of acetylene from calcium carbide and water is in accordance with the following equation :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The reaction is very rapid even in the cold and is accompanied by the liberation of a considerable amount of heat, 30·4 kg.-cal. per g.-mol.

The time necessary in practice for the decomposition of a given quantity of carbide is dependent upon the following factors :

(1) The relative proportions of water and carbide.
(2) The dimensions of the individual pieces of carbide.
(3) The degree of purity of the carbide and the nature of and orientation of the impurities.
(4) Degree of porosity.
(5) Method of bringing the carbide into contact with the water.
(6) The superficial area of calcium carbide exposed to the action of water.

If water is in excess, carbide which satisfies the normal commercial standard of purity will yield approximately 90% of its total gas yield within 60 seconds, and the remainder within a further 60 seconds, when the pieces are of approximately 15 mm. grading. Fine grades of the carbide, 1–2 mm., are entirely decomposed in under 3 seconds. Other things being equal porous carbide generates gas more rapidly than non-porous.

The evolution of heat must be controlled by providing means for heat absorption, such as the use of water in excess of carbide or by water-jacketing the apparatus, otherwise the resultant rise in temperature may cause total or partial polymerisation or decomposition of the gas. Other methods for controlling the rise in temperature include using moist solids for the decomposition of the carbide from which water is only slowly extracted as generation proceeds ; another method consists in coating the surface of the carbide with oil, tar compounded with sulphur, molasses, etc. For certain purposes the carbide is made less pure for the same reason. Fine dust carbide when brought into contact with water may become heated to the point of ignition and sometimes decompose with explosive violence.

Gas Yield from Calcium Carbide.

It is evident from the chemical equation expressing the decomposition of calcium carbide that 64 grms. of carbide yield theoretically 22·4 litres of acetylene, or 26 grms. This corresponds to 0·4062 lb. of acetylene per lb. of carbide or 406·2 grms. of acetylene per kilo. of carbide. The amount of heat released during this reaction is 475 kg.-cal. per kilo. or 4,380 B.Th.U. per lb.

The corresponding volume to this 0·4062 lb. of gas when measured at standard temperature (60°F.) and standard barometric pressure (30 in. mercury) is 5·907 cu. ft. As in the normal process of gas generation the gas is always saturated with water vapour, the corresponding volume is 6·016 cu. ft./lb. The influence of water vapour upon apparent volume must not be overlooked in any working process where nett acetylene only enters into the process.

These theoretical yields are, however, never obtained from the calcium carbide of commerce. The gas yields from such qualities depend upon the pure calcium carbide content and this figure is influenced by the extent of atmospheric attack which has taken place during crushing, screening, packing and general handling up to the time of use.

The smaller sizes of carbide which present a larger surface to the action of the atmosphere are more seriously attacked and therefore become "limed" on the surface prior to use, and for this loss of carbide allowance has to be made when calculating the yield of gas. This is shown by the following table taken from the B.S.I. Specification for Carbide of Calcium, No. 642, 1935.

Gas Yield.

"The standard graded sizes of carbide of calcium shall, when tested in accordance with Appendix A, yield the amounts of gas (measured dry or corrected to a dry gas basis) set out in the following table. Rights of claim or refusal in respect of gas yield shall be subject to the conditions set out in Appendix B.

For all sizes from	Cubic ft. per lb. at 60°F. and 30″ mercury.	Metric equivalent litres/kilo. at 15°C and 760 mm. mercury.
mm. mm.		
15 to 120	4·8	300
7 to 15	4·56	285
4 to 7	4·32	270
2 to 4	4·08	255
1 to 2	3·84	240

(Factor for conversion from cu. ft./lb. to litres/kilo. = 62·5.)"

The above table corresponds to commercial grades of carbide containing approximately 80% pure calcium carbide. Such carbide liberates a correspondingly smaller amount of heat during decomposition, *e.g.* an 80% quality carbide gives approximately 3,500 B.Th.U. per lb.

In addition to acetylene certain gaseous impurities are yielded during the chemical reaction between water and calcium carbide of commercial quality. Whilst it is usual to prescribe the limits of certain of the impurities such as sulphur and phosphorus compounds, which should not exceed 0·15% and 0·06% respectively when determined in a prescribed manner, a more complete analysis of the gas from an average commercial quality of calcium carbide gave the following results :

	% by volume.
Acetylene	up to 99·60
Oxygen	0·10
Nitrogen	0·10
Hydrogen	0·06
Hydrogen sulphide	0·10
Phosphine	0·05
Ammonia	Traces (but variable according to conditions of generation)
Carbon dioxide	0·20
Carbon monoxide	0·01
Methane	0·04
Silicon hydrides	0·010

Where the water is present in sufficient quantities during generation of gas some of these dissolve in, and are retained by, the water. Those impurities not scheduled and limited by the specification cited are of no importance, with the exception of the silicon hydrides which require careful consideration and control, as it is the view of some authorities that they are a potential source of danger, tending to cause or induce spontaneous ignition during the handling and use of carbide.

Pure acetylene has an odour akin to ether and is not at all objectionable. The characteristic odour usually associated with acetylene is due to the presence of impurities.

The permissible temperature of the mass of carbide and water during the reaction of decomposition must be kept within certain limits. The limits of temperature specified under safety regulations vary somewhat for different countries and largely depend upon the position in the apparatus where the temperature is taken. This temperature should never exceed the boiling-point of water, and the temperature of the gas on leaving the reaction chamber should be in the neighbourhood of 50°–60°C.

Excessive temperatures lead to polymerisation and/or dissociation of the acetylene and to the production of tarry matters, whereas temperatures which are too low generally result in reduced gas yields due to the higher proportion of gas dissolved in the water discharged from the apparatus. Temperatures of 36°C. and 65°C. should be regarded as the most suitable minimum and maximum limits. To ensure complete gasification of the carbide the residue should be completely converted to calcium hydroxide with water in excess.

The calcium hydroxide resulting from the reaction will always occupy a larger volume than the original calcium carbide, in fact usually three times as much, and proper space allowance must always be made for this in a gas-generating apparatus.

Such residue although a waste from the process of acetylene production has many practical uses as hydrate of lime. For many purposes calcium hydroxide from calcium carbide has a markedly greater activity than the calcium hydroxide made from calcium oxide by the ordinary process of slaking.

PERMISSIBLE PRESSURES IN ACETYLENE PRODUCING APPARATUS.

Acetylene is an endothermic compound and gives out its heat of formation immediately upon decomposition :

$$C_2H_2 = 2C + H_2 + 64 \text{ kg.-cal.}$$

Under ordinary pressures up to 1·5 atm. locally induced decomposition does not propagate, but if higher pressures are applied local decomposition is communicated to the whole mass with explosive violence. Such decomposition does not require the addition of either air or oxygen. For this reason the maximum pressure under which acetylene may be produced by gasification is limited by statute.

In Great Britain the limit of pressure is governed by an Order in Council issued under the Explosives Act, 1875, dated June 18, 1914, which declares as follows :

> "Acetylene—when subjected to a pressure above that of the atmosphere, capable of supporting a column of water exceeding 250 in. in height—shall be deemed to be an explosive within the meaning of the said act. Acetylene declared to be an explosive shall be prohibited from being manufactured, imported, kept, conveyed, or sold."

By an amending order now pending it may be permitted to raise the pressure to approximately 1·5 atm. gauge pressure outside the gasification apparatus or generator, subject to the approval by the appropriate State Dept. of the compressing apparatus and the processes whereby this increase in pressure is carried out.

The above limitation of pressure does not apply to compressed acetylene contained in a porous mass—Dissolved Acetylene—which is, subject to the prescribed conditions contained in the Order of the Secretary of State (No. 9), June 23, 1919, not deemed to be an explosive.

It is usual practice in Great Britain to generate the gas at pressures not exceeding 8–10 in. water column, although the regulations of the British Acetylene Association divide the apparatus into two classes, *i.e.* up to 60 in. water column and up to 250 in. water column—*see* B.A.A. Regulations relating to Acetylene Generation Apparatus. (*See* Statutory Rules and Orders, 1928—No. 992, Petroleum ; The Petroleum (Carbide of Calcium) Order, 1929.)

STORAGE OF CALCIUM CARBIDE.

Calcium carbide may only be stored in properly constructed and licensed stores as provided for by the Petroleum (Consolidation) Act, 1928. Licenses are issued by local authorities.

As there are no precise specifications for construction and design of carbide stores and as much is left to the discretion of the local licensing authorities, it is advisable to consult them before erecting a carbide store.

The main requirements are that the store shall be dry and well ventilated, that there shall be no possible ingress of water, rain or snow, that no naked flame or light shall be put or taken into the store, that if artificial lighting is necessary it shall be from outside or that flame-proof electric lamps are used. Also, there shall be no heating apparatus in or adjacent to the store, no water pipe or connection shall be inside the store, and the appropriate statutory notice and warning shall be properly displayed.

ACETYLENE GENERATION APPARATUS.

The design of such apparatus is to be entrusted to specialists only. The choice of a suitable design, size and type is dependent entirely upon the purpose for which the gas is to be used. Present-day types of generators range in capacity from small sizes taking a charge of a few ounces of carbide up to large sizes which take from one to ten tons according to requirements.

The principal object, of course, is to produce the maximum amount of gas from a given weight of carbide, with a minimum amount of gaseous impurities.

Temperature, pressure and avoiding admixture of air with the gas leaving the generators are the primary essential factors to be considered during the process of working and these may be summarised as follows :

(1) Control of temperature by dissipating the heat resulting from the chemical reaction between the carbide and the water.
(2) Control of pressure within the permissible limits.
(3) Complete gasification of the calcium carbide.
(4) Prevention of waste of gas due to excessive "after"-generation.
(5) Efficiency of safety devices for protection against excessive temperature and pressure.
(6) Storage accommodation for gas generated.

There are two main principles for bringing about and controlling evolution of gas :—

(1) Carbide is put into excess of water.
(2) Water is put on to excess of carbide.

In the first method the amount of gas generated is controlled by the rate of feed of carbide, and the excess of water, which controls the temperature, may or may not be simultaneously replenished according to the size and type of apparatus.

In the second method the amount of gas generated is controlled by the rate of water feed and this process of production usually results in the gas having a high temperature which necessitates it being subsequently cooled. The generation chamber is cooled by water-jacketing or the rate of generation is so retarded that the heat liberated is dissipated by radiation and conduction.

The first method is the only one suitable for use where large quantities of gas are required, the second method is suitable for small plants or portable apparatus but is not of great technical importance.

The use of large plants working by the second method for very small demands of gas leads to overheating of the carbide in the generation chamber and polymerisation of the gas as indicated by a yellowish-brown residue smelling of tar.

The modern trend is for larger plants with high rates of generation, for which designers adopt the first or carbide-to-water method.

There is also an intermediate type which works on what is called the contact method, whereby the carbide is contained in a bucket or equivalent receptacle and is from time to time dipped into a mass of water and then withdrawn according to the requirements for gas. Such apparatus is not favoured for technical purposes; its only virtues are cheapness and compactness, but it is usually wasteful in gas due to the necessity of releasing surplus, and further it gives rise to very high temperatures in the mass of carbide in the generation chamber.

A mechanical equivalent is the displacement type in which, dependent upon the variations in pressure due to variations in demand, water is allowed to come in contact with the carbide and as gas is generated water is forced back into a reservoir. This has the same disadvantages as the contact type.

Both of the latter types are discouraged for technical purposes because of their low efficiency, indifferent gas yield, and also because of the comparatively high explosion hazard when opening out for recharging.

The possible modifications in mechanical arrangements for bringing the water and the carbide into contact for the purpose of gas generation are legion, and it is only necessary to illustrate and describe a few examples.

The construction of a typical low-pressure water-to-carbide generator may be seen in the illustration, Fig. 1.

Carbide is loaded into trays at the bottom of the plant, the quantity varying from 7 to 75 lb. according to the size of the apparatus, and the tank is filled with water. When the gasholder is down, that is, empty, the water control valve is open and water is allowed to drop on to the carbide in the trays. This causes acetylene to be generated and hence the gasholder rises ; when it has risen above a certain point, the water control valve is automatically closed and no further acetylene is generated until the quantity of gas within the holder has been so far decreased as to cause the holder to fall once again below the point at which the control valve opens. Such a plant is ideal for a small workshop, for a garage, or in any shop which is doing intermittent work and which requires anything from 5 to 150 cu. ft. of acetylene per hour. As can be seen, it incorporates many advantageous features. It is compact in design, yields acetylene at constant pressure, is simple in construction, and the generating chambers are water-cooled.

The water-to-carbide principle is adopted in most small and medium-sized generators, also in flare-lights, hand-lamps, bicycle lamps, etc.

A typical generator of the carbide-to-water type is represented by the accompanying illustration, Fig. 2. As may be seen, carbide is fed into a large hopper, whence it is slowly transferred via a chute by means of an endless helical screw into the body of the generator. The latter is partially filled with water and hence the carbide is decomposed on its passage downwards.

Sludge, that is, calcium hydroxide, falls to the bottom of the generator, and may be run off from time to time, whilst hard metallic inclusions are retained on a wire grid which is mounted on a central shaft. In the latest designs of such plant the worm feed is electrically driven and there is an automatic flushing system for replenishment with water and removal of sludge. The hopper is capable of holding up to 1 ton of carbide and the generator 500 gallons of water. The average consumption of carbide is about 2 cwt. an hour and the yield on an average 1,000 cu. ft. per hour. The most efficient method of running such a generator has been found so to regulate the water feed and carbide supply that the gas is maintained at a fairly high temperature, about 60°C. In

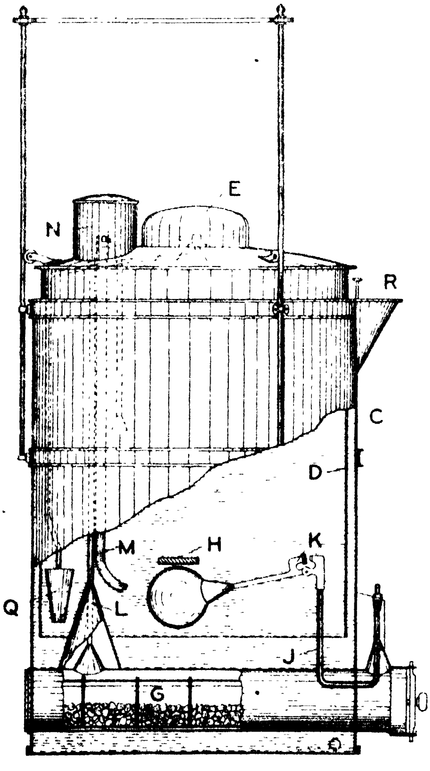


Fig. 1.—Water-to-Carbide Generator.

this way losses due to solution of acetylene in the water are reduced to a minimum.

Generators working on the principles just described and producing about 1,000 cu. ft. per hour are usually only to be found in factories producing dissolved acetylene. The gas is not consumed on the spot but is compressed into steel cylinders and delivered for use to customers' workshops.

DISSOLVED ACETYLENE.

The gas leaving the generator is not immediately suitable for compression, and must first pass through a series of washing, purifying and drying operations. The various stages may be seen from the illustration, Fig. 3.

The gas is first cooled, washed free from ammonia, passed into a gasholder, metred and then enters the purifying chambers, where by means of suitable chemicals it is freed from hydrides of sulphur, phosphorus, silicon and all other impurities.

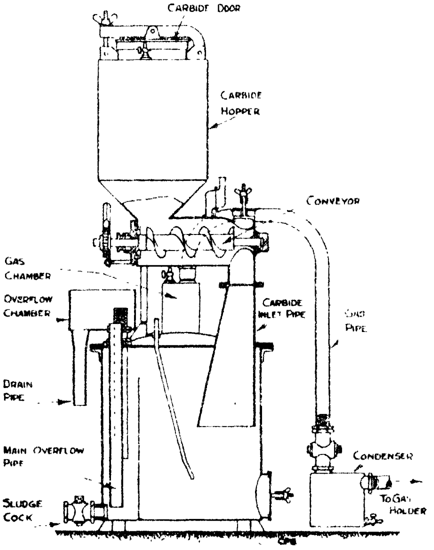


FIG. 2.—Carbide-to-Water Generator.

The purifying materials used for the removal of these impurities are usually of an oxidising nature, such as chromic acid or ferric chloride in association with small quantities of catalysts, such as salts of copper or mercury, with the whole of which a porous body such as calcined kieselguhr is impregnated. There are two types of purifying material, regenerative and non-regenerative. As the name implies, the latter type can only be used once and when exhausted must be thrown away; an average sample of such material will purify approximately 200 cu. ft./lb., whereas the regenerative type will give a similar purification value and if exposed to the atmosphere will regenerate, a change which may be observed visually by the colour transformation, colourless (spent) → brown (active), and may then be used over again. This cycle of processes may be repeated six or seven times without any marked decrease in purifying activity. The total purifying value so obtained is of the order of 1,500 cu. ft./lb. The enormous saving in materials, time, and labour when using such a purifying mass is at once evident.

The gas is next thoroughly dried by means of calcium chloride driers and passes on to the compressors. These are usually of the three-stage direct-drive type, capacity 250–1,000 cu. ft./hour, and compress the acetylene up to 225 lb./sq. in. The gas after leaving the compressors is again dried and passes on to filling racks, to which are attached the cylinders. The cylinders used for the storage of acetylene are known as D.A.—"Dissolved Acetylene"—cylinders, and differ considerably from the cylinders commonly used for the storage of commercial gases. As is well known, acetylene is a gas which is comparatively easily liquefied: b.p. −82·4°, critical temperature 37°, critical pressure 67–68 atmospheres, and at 0° the liquid

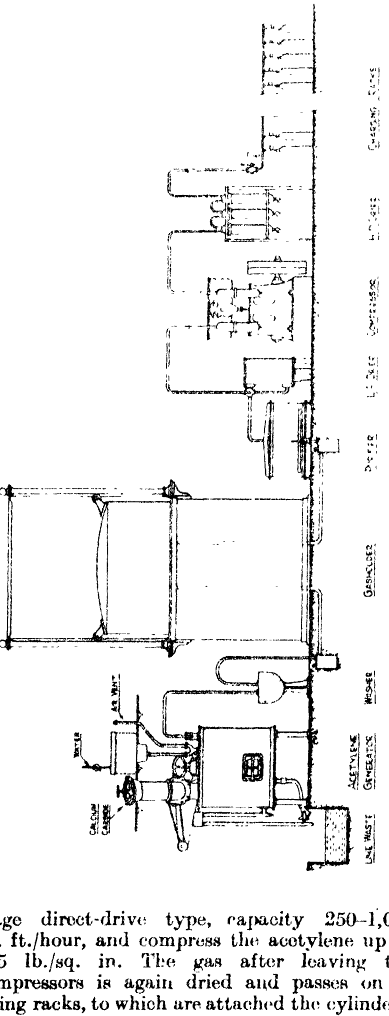


FIG. 3.—Illustration of Lay-out of Plant.

has a vapour pressure of about 25 atmospheres ; hence it would be a comparatively simple matter to liquefy the gas by compression at ordinary temperature and so transport it in the solid or liquid state; but owing to its extreme instability in the liquid and solid states, the use and transport of acetylene in the liquid or solid condition for commercial purposes is forbidden by law. However, by an Order in Council, which has been previously mentioned, acetylene is under certain conditions exempted from the Explosives Act and it is now permissible to compress acetylene up to a pressure of 15 atmospheres at 60°F. into cylinders, provided that the cylinders are themselves filled with an officially approved porous material and the charging is effected under approved conditions.

The primary object of the porous mass is to divide the internal space of the cylinder into a very large number of very small cells, so that in the event of any ignition, decomposition is merely local—there must be no propagation of either flame or explosion throughout the whole mass. The requirements that such a mass must fulfil are necessarily very stringent. The material must be light, extremely porous, non-inflammable; it must completely fill the cylinder, leaving, of course, the requisite amount of free space as laid down in the Home Office decree, but allowing no voids, gaps or air pockets; it must withstand shock, friction, heat, the action of acetone, acetylene and any impurities which might possibly find their way into the cylinder. Further, the mass must show no tendency to sink or sag in use and, finally, its density must be such that when tightly filled into a cylinder there still remains approximately 80% of the total internal volume of the cylinder unoccupied by solid matter. It might be thought that such a mass would be difficult to obtain, but many materials have been proposed, such as wood charcoal, kapok, pumice, silica, sawdust, etc., and adopted to varying degrees.

The materials most in use in this country are kapok and charcoal. Kapok is a vegetable fibre from the pods of the tree *Ceiba pentandra* which flourishes in Java and the East Indies. It is a cream-coloured resilient material, resembling cotton wool in appearance and composed of a mass of very fine hairs about 10–15 mm. in length and about 0·02 to 0·03 mm. in diameter. The charcoal used is a high-grade hardwood charcoal in granulated form and combines the properties of a highly sorptive carbon with the hard and durable properties of the wood from which it is made.

In order to increase the storage capacity of the cylinders, a liquid solvent is introduced and the acetylene dissolved under pressure. The solvent in universal use is acetone, a colourless, pungent, volatile organic liquid, b.p. 56°C., and the best known solvent for acetylene. One volume of acetone will dissolve about 25 volumes of acetylene under normal temperature and pressure, and the advantage accruing from its use will be appreciated when it is considered that 1 cu. ft. of acetone will dissolve 275 cu. ft. acetylene under a pressure of 15 atmospheres.

From what has been said it will be realised that the interior of a D.A. cylinder is not quite as simple as is usually thought. But there is one more complicating factor. Acetone, on dissolving acetylene, expands considerably, so that one litre of acetone which is saturated with acetylene increases 4% in volume for each rise of 1 atmosphere in saturation pressure.

This means, in effect, that 1 litre of acetone when saturated with acetylene at 15 atmospheres pressure will occupy approximately 1·6 litres.

Further, the solution has a coefficient of thermal expansion equal to 0·0015, so that precautions must be taken that, within the temperature variations likely to be experienced the quantity of solid, liquid and gaseous material within the cylinder is such that at no time can the liquid content exert a hydraulic pressure. In practice, in this country, these conditions are met by having 20% of the internal volume occupied by a solid matter, 40% occupied by liquid at 60°F. and before solution of gas, and a maximum charging pressure of 225 lb./sq. in. at 60°F.

For example, a "100 ft. D.A. cylinder" which has a water capacity of 1 cu. ft. would contain 18 lb. of porous mass having a specific gravity of 1·5, and about 20 lb. of a solvent having a specific gravity of 0·8. The weight of gas contained at 15 atmospheres pressure would be about 7 lb. (1 cu. ft. acetylene=1·1 oz. at 60°F.), for it should be observed that on a commercial scale the acetone is never completely saturated.

APPLICATIONS OF ACETYLENE.

1. WELDING.

By far the most important field of application is found in the welding industry. A weld has been defined as a "union of two or more pieces of metal effected while the surfaces joined are in the liquid and/or plastic state," and hence some source of intense local heating is required for the harder metals and alloys to bring the surfaces to the liquid or plastic state. The oxy-acetylene flame supplies the necessary heat.

Combustible Properties.—Acetylene is one of the most powerful combustibles known. Its formation is represented by an endothermic reaction, that is, energy in the form of heat is absorbed during formation and, hence, when acetylene is decomposed by combustion this heat of formation is given out in addition to the normal heat of combustion of its constituents. Thus :

$$\begin{array}{llr} C_2H_2 \rightarrow 2C + 2H & & +\ 64 \text{ kg.-cal.} \\ 2C + O_2 \rightarrow 2CO & & +\ 58 \text{ kg.-cal.} \\ 2CO + O_2 \rightarrow 2CO_2 & & +138 \text{ kg.-cal.} \\ 2H + O \rightarrow H_2O & & +\ 60 \text{ kg.-cal.} \\ \hline C_2H_2 + 5O \rightarrow 2CO_2 + H_2O + 320 \text{ kg.-cal.} & & \end{array}$$

from which it is seen that 26 g. of acetylene yield 320 kg.-cal., or stated in the manner usually adopted in industry, acetylene has a calorific value of about 1,500 B.Th.U., compared with 500 in the case of coal gas and 350 in the case of hydrogen.

This heat is utilised commercially in the oxy-acetylene blowpipe flame. Acetylene is burnt in oxygen by means of a specially constructed blowpipe and flame temperatures well above the melting-points of the majority of metals and alloys are obtained.

It is extremely difficult to give an accurate value for the temperature of the oxy-acetylene flame for two reasons. Firstly, the temperature attained is considerably higher than the melting-points of most of the metals, alloys, refractories, etc., such as are employed in the construction of thermocouples, segar cones, etc. The second difficulty in stating the temperature of the acetylene flame lies in defining the prevailing experimental conditions. The values found depend on many factors, *e.g.* the hygrometric state of the gas, whether partially or completely saturated with water, the presence of other gaseous or liquid constituents, such as acetone, hydrides of phosphorus and sulphur, the pressure and purity of the oxygen used for combustion, and the shape and type of burner used.

However, it may be said with certainty that the temperature at the tip of the white cone in an oxy-acetylene flame, when using a correctly constructed and regulated oxy-acetylene blowpipe, is about 3,500°C.

As may have been observed, the combustion of acetylene takes place in two distinct stages and these two stages may be seen clearly in the ordinary oxy-acetylene flame. The flame consists of a small inner blue-white cone, surrounded by a less sharply defined bushy envelope. In the central cone, acetylene dissociates into its elements, yielding carbon and hydrogen :

$$C_2H_2 \rightarrow 2C + 2H$$

and the carbon is next oxidised to carbon monoxide :

$$2C + O_2 \rightarrow 2CO$$

whilst in the outer envelope the final stage of oxidation is completed, giving carbon dioxide and water :

$$H_2 + O \rightarrow H_2O$$
$$CO + O \rightarrow CO_2$$

It is seen from the equation

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

that two volumes of acetylene require five volumes of oxygen for complete combustion, but in welding practice it is found that it is not necessary to supply the theoretical quantity of oxygen to the burner in order to obtain the most efficient flame, and usually the gases are mixed in the ratio 1 : 1, the remaining oxygen being taken from the surrounding atmosphere.

The plant required for oxy-acetylene welding depends on whether the low-pressure or the high-pressure system is adopted.

In the first case it is necessary to have a low-pressure generator of suitable dimensions, hydraulic back-pressure valve, oxygen cylinder and regulator, and a low-pressure oxy-acetylene blowpipe. In the second case it is necessary to have a cylinder of dissolved acetylene and regulator, oxygen cylinder and regulator, and a high-pressure oxy-acetylene blowpipe. If the low-pressure system is adopted and the acetylene pressure is insufficient for a satisfactory welding flame it must be boosted up. This may be effected by fitting an injector in the blowpipe, high-pressure oxygen being used to induce the acetylene, and so give the necessary pressure at the burner orifice. The construction of such a blowpipe may be seen from the illustration (Fig. 4) and data can be found in the table giving the thicknesses of metal which may be welded as well as the consumption of gases.

The blowpipes are provided with a series of interchangeable tips, covering a wide range of sizes, so that for each thickness of metal to be welded the corresponding blowpipe tip may be fitted.

LOW-PRESSURE SYSTEM.

Thickness metal to be welded.	Regulator pressure. O_2	Approx. consumption of gases per hour C_2H_2	O_2	Approx. speed of welding.
inches.	lb /sq. in.	cu ft.	cu. ft.	ft /hour.
1/64—1/32	7	1·25	1·5	—
1/32—3/64	10	2·75	3·25	—
3/64 1/16	10	3·5	4·25	16
1/16 3/32	13	6	7·25	12
1/8—3/16	15	12	15	9
1/4—5/16	20	20	25	8
3/8—7/16	25	28	35	6
1/2—9/16	32	39	47	4

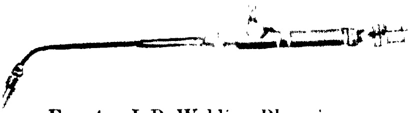


FIG. 4.—L.P. Welding Blowpipe.

The object of the hydraulic back-pressure valve is to preclude the possibility of any backfire returning to the gasholder of the acetylene generator, and this valve is essential with all injector type blowpipes. It will be observed that the necessary oxygen pressures for any particular thickness of metal are greater in the case of the low-pressure system than in the case of the high-pressure system.

If dissolved acetylene is used the blowpipe is much simpler in construction, since the gas is stored under pressure and an injector is no longer necessary, it being sufficient to have a reducing valve fitted to the cylinder pressure gauge.

Typical blowpipes may be seen in the illustration (Fig. 5) and data concerning the size of tip, gas consumption, etc., will be found in the table.

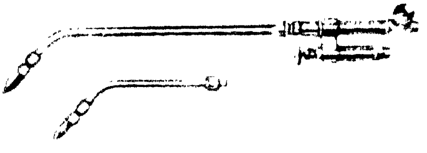


FIG. 5.—H.P. Welding Blowpipe.

HIGH-PRESSURE SYSTEM.

Thickness metal to be welded.	Regulator pressure. C_2H_2	Regulator pressure. O_2	Approx. consumption of gases per hour. C_2H_2	Approx. consumption of gases per hour. O_2	Blowpipe tip.
inches.	lb./sq. in.		cu. ft.	cu. ft.	Litres.
up to 1/32	2	4	0·89	Same as acetylene	25
1/32	2	4	1·75		50
1/24	2	4	2·66		75
1/16	2	4	3·50		100
1/12	2	4	5·25		150
1/8	2½	4½	7·75		225
3/16	3	5	12·25		350
1/4—5/16	4	7½	17·25		500
5/16—1/2	5	10	25·00		750
9/16—1	7½	15	36·00		1,000

Methods of Welding.—In order to effect a weld it is necessary to heat the edges of the metal to be joined until they melt ; the molten metal runs together, and on cooling a homogeneous joint or autogenous weld is produced.

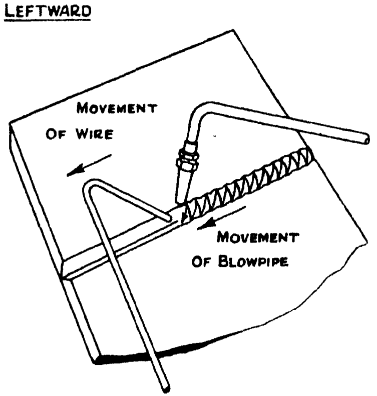


FIG. 6.—Leftward welding.

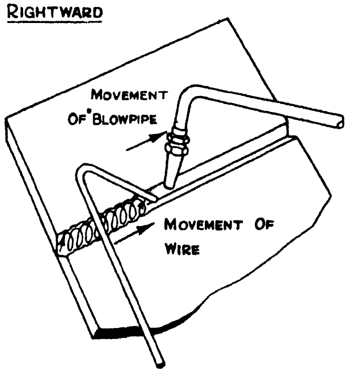


FIG. 7.—Rightward welding.

This simple procedure is sufficient for thin sections of metal, not greater than $\frac{1}{16}$ in. in thickness, but for thicker sections it is necessary to add additional metal in the form of a welding rod. There are two methods of welding, the normal or "leftward" method and the "rightward" method.

Leftward Method.—This method of welding was the first to be developed and is still extensively used. As may be seen from the illustration (Fig. 6), the weld is commenced on the right-hand side of the join and the direction of advance is to the left. The welding rod precedes the blowpipe, the nozzle of the latter pointing in the direction of the unwelded joint. The blowpipe is given a semi-rotatory forward motion, whilst the rod is given a steady forward motion. The rod is inclined at an angle of 30°–40° to the plate, whilst the blowpipe is inclined at an angle of 60°–70°. This method is quite satisfactory for thicknesses of plate up to $\frac{3}{16}$ in. but over that thickness the method becomes uneconomical, due to the high consumption of gases, rapid decrease in speed of welding and an increased tendency to over-heating.

Rightward Method.—A comparatively recent modification of oxy-acetylene welding technique is the method of "Rightward Welding." In this case the weld is commenced on the left-hand side and welding proceeds from left to right. As may be seen (Fig. 7), the blowpipe precedes the welding rod and the blowpipe flame points in the direction of the completed weld. The rod is inclined at an angle of 40°–50° to the plate and the blowpipe at a similar angle. This method is applied to all sheet over $\frac{3}{16}$ in. in thickness and has many advantageous features when compared with the normal or leftward method. It is very much more rapid, is more economical in gases and welding rod, and gives rise to excellent mechanical properties in the finished weld.

New Butt Welding Techniques for Steel.—During recent years a number of new techniques for the butt welding of steel have been introduced and these new techniques have been the means of decreasing the cost and increasing the efficiency of the oxy-acetylene welding process.

The two most important methods are the Vertical method and a method known as Linde-welding.

Vertical Welding.—As the name implies, this method which is an extension of the Leftward Method requires that the plates to be welded be arranged in a vertical position. Up to plate thickness of $\frac{3}{16}$ in. one welder only is employed and it is unnecessary to bevel the edge of the plate. The weld is commenced at the bottom of the plate and the weld is made from bottom to top.

For plate thicknesses greater than $\frac{3}{16}$ in. it is an advantage to use the two-operator method of vertical welding. By this method two welders are employed working from opposite sides of the plate. It is necessary that the welders work at exactly the same speeds, but once men have been trained in this method the speed of welding is increased far beyond that which could be obtained by any other method of oxyacetylene welding on the same thickness of plate.

Complete penetration of the weld seam is obtained, adhesion is impossible and there is an equal deposit of weld metal on both sides of the weld seam. There is also a saving in fuel gases and welding rod.

Lindewelding.—This method of welding embodies principles which are quite different from those applied in ordinary welding and it is at the moment of fairly limited application.

The flame used is a carburising flame, that is, it has an excess of acetylene. The metal is not completely fused but is brought to incipient fusion.

The fundamental idea of the method is that the excess of acetylene in the flame causes a slight absorption of carbon by the surface of the heated steel. This lowers the melting-point and so a weld may be carried out at a temperature lower than the melting-point of the metal being welded. It is essential when Lindewelding to use a welding rod which contains slag forming elements such as silicon and manganese which reduce surface oxide.

Lindewelding can be considered as an extension of the Rightward method of welding because the welding rod precedes the flame, and welding proceeds from left to right.

The advantages claimed for the method include an increase in welding speeds and a decrease in welding costs. The method is limited, however, to welds in a horizontal plane and for the welding of pipe joints arrangements must be made to rotate the pipe.

Welding Rods and Fluxes.—The composition of the filling rod is usually approximately the same as that of the material to be welded, but often includes small quantities of special alloying elements, such as silicon, manganese, phosphorus, etc., which facilitate the manipulation of the molten bath of metal, increase fluidity, and improve the mechanical properties of the resultant weld. The diameter or gauge of rod used depends upon the thickness of sheet to be welded, but for the oxy-acetylene process when welding mild steel, wires smaller than 16 S.W.G. or greater than $\frac{3}{8}$ in. diameter are rarely used. If materials other than mild steel are to be welded, such as aluminium, copper, brass, bronze etc., a flux is usually necessary. The purpose of the flux is to dissolve scale, promote fluidity and to ensure that a clean sound joint free from non metallic inclusions is obtained. Most fluxes are in powder form, those for use with copper and copper alloys such as brasses having a borax or boric acid base, while those intended for use with aluminium and similar light alloys usually have an alkali halide base such as the chlorides and fluorides of lithium, sodium, and potassium.

It may be mentioned at this stage that D.A. cylinders, hose, equipment and, in fact, any plant connected with acetylene are coloured maroon red and screwed fittings have left-hand threads; while cylinders, hose, plant, etc., dealing with oxygen are painted black and screwed fittings have right-hand threads.

Extent and Scope of Oxy-Acetylene Welding.—The process is used in the welding of practically all metals and alloys ; welds are regularly carried out on all types of steel, aluminium, brasses, copper, monel metal, nickel, lead, cast iron, stainless steel, German silver, etc., and also on the many alloys which have been recently developed, such as *elektron*, *birmabright*, *tungum*, etc.

There are now few trades and industries in which welding does not play a part. It is employed in such manufacturing processes as the production of boilers, tanks, automobile parts, furniture, agricultural implements, dental goods, ornamental brassware, aeroplane parts, machine tools, scientific instruments, etc., or as a constructional medium in the laying of pipe-lines for oil, steam, gas, water, etc., in the binding of steel rails, or in the building of steel structures. It is perhaps of interest to note that gold dust is subjected to a preliminary cleaning by the air-acetylene flame. In addition to the production of new articles there is, of course, the extensive field of repair work, a field which covers almost everything from the building up of a ten-ton casting to the repair of a dental plate.

2. OXY-ACETYLENE CUTTING.

Next in importance to welding comes oxy-acetylene cutting, a process which, originally introduced merely for demolition work, finds wider application every day. The principle underlying metal cutting by the oxy-acetylene process is that of extremely rapid oxidation of the metal assisted by the mechanical effect of a blast of oxygen directed into the molten metal. The metal is first raised to a red heat by an oxy-acetylene flame and a jet of oxygen is then directed on to the hot metal. The heat generated by the process of oxidation is then sufficient to fuse the metal, and by slowly drawing the blowpipe across the sheet the fused metal is removed by the cutting effect of the oxygen and a clean cut is obtained.

The blowpipes necessary for this operation are not the same as those used for welding. The cutting tip contains a central orifice for the "cutting oxygen supply" and an annular orifice for the "heating oxygen" (Fig. 8).

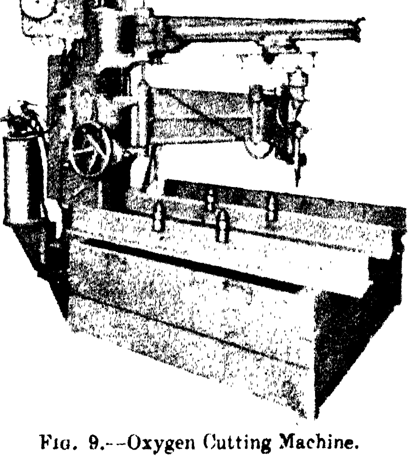


FIG. 9.—Oxygen Cutting Machine.

The principle of the simple hand-cutter shown has been applied to cutting machines. These machines are extensively used for repetition cutting work in conjunction with appropriate templates. A typical machine shown in Fig. 9, fitted with electrical drive and magnetically operated template, will cut any thickness of steel plate from ⅛ in. to 6 in., giving a circular cut up to 20 in. in diameter and a straight cut up to 4 ft. in length.

Oxy-acetylene cutting is confined to ferrous materials, chiefly mild steel, but much progress has been made recently in the development of cast iron cutting. A special technique has been evolved and no doubt the method will attain still greater importance in the near future.

Hand-Cutting Steel.

Thickness material.	Speed of cutting.	Gas consumption.	
		Oxygen.	Acetylene.
inches.	ft./hour.	cu. ft./hour.	cu. ft./hour.
¼	70	42	16
½	60	50	20
1	48	150	24
2	30	190	28
6	15	270	43

3. Surface Hardening.

Another important application of the blowpipe is found in the surface treatment of metals. It is a well-known fact that steels, provided they have a suitable carbon content, may be hardened by first heating to a known temperature and then suddenly cooling. However in practice it is often difficult to attain the right degree of local heating when the usual methods of heating are adopted, and a process has been developed using the intense local heating action of the oxy-acetylene flame. The appliance to be surface hardened, for example, a large gear-wheel, is mounted in a water tank so that it may revolve with almost the whole of the gear immersed in cold water, and only a portion of one tooth, the part to be hardened, exposed. The flame of a blowpipe is then directed on to the tooth, and if the steel does not contain sufficient carbon, it is first carburised by treating with an oxy-acetylene flame containing an excess of acetylene. The tooth is then heated to the required temperature and immediately immersed in the quenching medium. This process, which can be applied to gears, cams, shafts, pulleys, etc., may be either hand-operated or mechanically controlled.

4. Hard Surfacing.

Another process for the surface treatment of metals is that of hard surfacing. By this process steel surfaces which are required to stand extensive shock, friction, abrasion or corrosion are heated until the metal begins to "sweat"—not until it melts—and then a deposit of hard surfacing material, usually alloys of cobalt, chromium and tungsten or molybdenum, is laid down by means of an oxy-acetylene blowpipe. The process finds wide application for the treatment of punches, dies, rock drills, excavators, agricultural implements, and on any surface which must combine strength and toughness with resistance to corrosion and hardness.

5. Lead Burning.

A process analogous to oxy-acetylene welding but having many important differences is that of lead burning and the homogeneous deposition of lead. For this purpose a special lead-burning blowpipe is used, much smaller than the normal oxy-acetylene blowpipe, since extreme delicacy of touch is required for much lead-burning work. The process is extensively employed by plumbers and is used in the chemical industry where extensive corrosion is encountered, for example, the familiar "lead chambers" used in the manufacture of sulphuric acid.

6. Illumination.

The use of acetylene as an illuminant is very interesting, for it was mainly due to the striking properties of acetylene as a lighting medium that the commercial production of calcium carbide was ever undertaken in earnest. The acetylene flame when supplied with the correct proportion of air shows a clear white light. The light is the nearest artificial approach to sunlight known, and does not contain a predominance of red and infra-red rays—its purity may be realised when it is remembered that it has been proposed as a standard illuminant to replace a *n* pentane lamp—and some years ago acetylene was widely used for lighting purposes in houses, vehicles, shops, etc. At the present time there are many thousands of marine buoys, searchlights, lightships, signalling lamps, etc., constantly in use which depend for their lignt on acetylene. By the use of specially constructed burners, which are so designed that the flame burns a short distance from the orifice of the burner, it is possible to ensure a "storm-proof" light which is quite unaffected by atmospheric conditions. Acetylene flares whether in use at docks, harbours, railway sidings, burst water mains, road repairs, etc., are a familiar sight to everybody and need little by way of description. Acetylene, which may be taken from a D.A. cylinder or from a small generator, is burnt at the orifice of a steatite burner and, according to size, will give a light varying from 50 to 3,000 candle-power. The illustration shows a multiple purpose outfit (Fig. 10). As the name implies, the plant may be taken to a breakdown job at night and the same acetylene cylinder be used for general lighting, local lighting on the part to be repaired, and also to supply acetylene to the welding blowpipe for repairing the breakdown.

7. Metal Spraying.

The process of protective metal coating, or metal spraying, as it is called, consists of feeding the metal to be sprayed in the form of a wire through the hot zone of an annular blowpipe. The flame used is an oxy-acetylene flame, and it immediately melts the wire. Before the metal can form into drops, however, it is picked up in a stream of compressed air at a pressure of about 45 lb./sq. in., atomised and deposited in a very fine layer approximately 0·002 in. thick on the surface to be covered (Fig. 11). The wire used is usually 1 mm. diameter, and the rate of depositing on an average 2 lb./hour. This varies naturally with the metal employed, it being possible to lay down more of a low melting-point metal such as zinc (6 lb.) than in the case of a high melting-point metal such as nickel (2 lb.). Recently high-speed metal spraying nozzles have been introduced using 2 mm. wire and depositing, in the case of zinc, up to 12 lb. of metal in an hour.

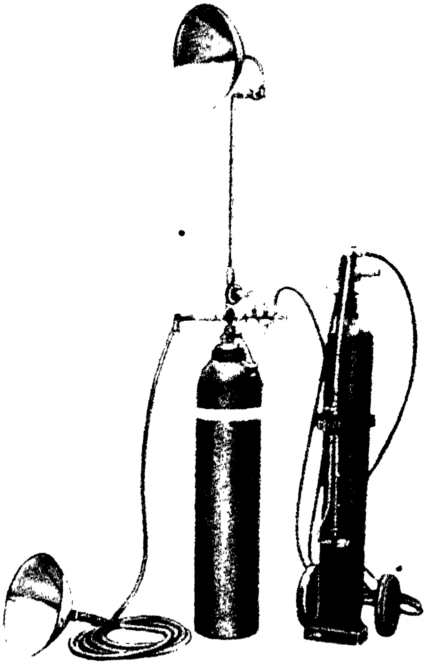


FIG. 10.—Multiple Purpose Outfit.

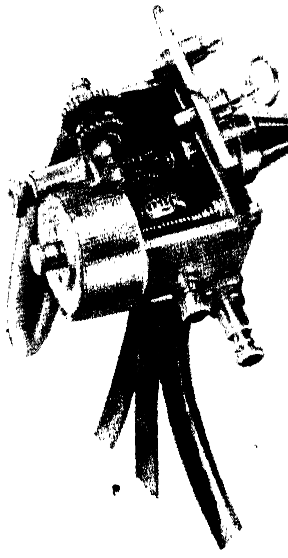


FIG. 11.—Metal Spraying Pistol.

Practically all metals may be deposited by this process and it has found widespread application during recent years for the protection of pylons, tanks, gasholders, chemical plant of all types and descriptions ; it has been used not only on metals but also on paper, wood, glass, asbestos, etc.; in fact, there seems to be no limit to the possible applications of the process.

8. POWER PURPOSES.

Another field has recently been opened up for acetylene in the automobile industry. Coal gas is at present being used on heavy motor vehicles to replace petrol for internal combustion engines, but has not a sufficiently high thermal value to give very satisfactory results. This deficiency can be made good by the addition of acetylene and in view of the possibility of difficulties arising in the supply of petroleum it may well be that this field of application will form an extremely important extension in the future of the acetylene industry. A. S. and N. D.

ACETYLENES, C_nH_{2n-2}. The compounds of this group comprise acetylene and its mono- and di-substituted derivatives. They are for the most part prepared by the action of alcoholic potash (often, conveniently, sodamide) on olefin dihalides, $RCHX{\cdot}CHXR'$, monohalogeno-olefins, $R{\cdot}CX : CH{\cdot}R'$, or ketone chlorides, $RCH_2{\cdot}CCl_2R'$ ($X = Cl, Br, I$).

$$RCHX{\cdot}CHXR' + 2KOH \rightarrow RC{:}CR' + 2KX$$

$$RCH_2{\cdot}CCl_2R' + 2NaNH_2 \rightarrow RC{:}CR' + 2NaCl + 2NH_3$$

Alkyl- and aryl-acetylenes can usually be prepared by the action of alkyl halides or esters of *p*-toluenesulphonic acid on the sodium derivative of acetylene or its homologues ; in the reaction between sodium acetylide and alkyl halides liquid ammonia has been successfully used as a medium. Alkylacetylenes have also been obtained by the action of calcium carbide on the vapours of alcohols at temperatures above 100°, and by the electrolysis of the salts of unsaturated dibasic acids :

$$KO_2C{\cdot}CR : CH{\cdot}CO_2K + 2H_2O \rightarrow RC{:}CH + 2KHCO_3 + H_2$$

Properties.—Acetylene and methylacetylene are gases at room temperature ; the succeeding members are liquids of characteristic acetylenic odour. The following, *inter alia*, have been isolated in pure condition :

Alkyl- and Aryl-Acetylenes

($CR{:}CH$ and $CR{:}CR'$).

Substituents.	B.p. (°C.).
Methyl	−23·3
Ethyl	8·6
n-Propyl	48–49
*iso*Propyl	28–29
n-Butyl	70·5–72
n-Amyl	99
Methyl-*n*-butyl	111–113

Substituents.	B.p. (°C.).
Ethyl-*n*-propyl	105–106
Methyl-*n*-amyl	133–134
Ethyl-*n*-butyl	131–132
n-Hexyl	131–132
n-Heptyl	160
n-Octyl	80–82 (27 mm.)
n-Nonyl	210–215
n-Decyl	95–97 (15 mm.)
Dimethyl	28
Methylethyl	55·5–56
Methyl-*n*-propyl	83–84
Methyl-*n*-hexyl	161
Ethyl-*n*-amyl	155–157
n-Propyl-*n*-amyl	74–75 (19 mm.)
Di-*n*-amyl	103–104 (14 mm.)
Phenyl	140·5
Benzyl	69·5 (18 mm.)
Methylphenyl	185
Diphenyl	m.p. 60

All the mono-substituted acetylenes, $RC\vdots CH$, possess one hydrogen atom which is replaceable by metals, and are known as true acetylenes; the di-substituted acetylenes, on the other hand, contain no such replaceable hydrogen atom in the molecule. Owing to the replaceable hydrogen atom, the mono-substituted derivatives can, like acetylene itself, form metallic derivatives (acetylides) with metals: the sodium derivatives, $RC\vdots CNa$, are readily formed from the hydrocarbons by interaction with sodamide or sodium, and the silver, cuprous and mercuric derivatives by interaction with ammoniacal solutions of silver and cuprous salts and aqueous suspensions of mercuric oxide, respectively. The hydrocarbons can usually be regenerated in pure condition from their silver or cuprous derivatives by the action of warm hydrochloric acid, and this affords a means of isolating and purifying the acetylenes. The mercuric derivatives of the general type $(CR\vdots C)_2Hg$, formed by the action of potassium mercuri-iodide (or mercuric cyanide and potassium hydroxide) on the hydrocarbons, are usually crystalline substances of sharp melting-point which can be used for identification purposes. By the interaction of metallic acetylides with reagents such as acetyl chloride, carbon dioxide or orthoformic ester, acetyl-, carboxy-, dialkoxy-methyl-, etc., derivatives of acetylenes can be obtained.

The mono-substituted acetylenes react with Grignard reagents to yield acetylenyl magnesium halides, which are of considerable value in synthesis:

$$RC\vdots CH + EtMgBr \rightarrow RC\vdots CMgBr$$

With iodine dissolved in liquid ammonia, their sodium derivatives (sometimes the hydrocarbons themselves) react to form iodoacetylenes, $RC\vdots CI$; with arylsulphonyl chlorides their sodium derivatives yield the corresponding chloro-derivatives. The reactive hydrogen atoms of the mono-substituted acetylenes are replaced by halogen when the hydrocarbons react with alkaline hypoiodite, hypobromite or hypochlorite.

The foregoing reactions depend on the replacement of acetylenic hydrogen atoms by other atoms or groups and cannot therefore apply to di-substituted acetylenes. There are, however, numerous addition reactions which apply to all acetylenes. On catalytic reduction the acetylenes yield in turn olefins and paraffins; also they unite with one or two molecules of halogen or hydrogen halide to yield addition products:

$$RC\vdots CR' \xrightarrow{Cl_2} RCCl:CClR' \xrightarrow{Cl_2} RCCl_2{\cdot}CCl_2R'$$

$$RC\vdots CR' \xrightarrow{HBr} RCBr:CHR' \xrightarrow{HBr^{\bullet}} RCBr_2{\cdot}CH_2R'$$

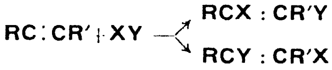
With hypochlorous or hypobromous acid reaction usually proceeds directly to the di-addition stage, with formation of the corresponding ketone:

$$RC\vdots CR' \xrightarrow{2HClO} RCO{\cdot}CCl_2R'$$

In certain cases which have been examined chlorine dissolved in methyl alcohol (equivalent to methyl hypochlorite) reacts additively with acetylenes to yield dichloro-dimethoxy-derivatives (ketals):

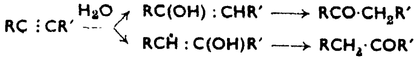
$$PhC\vdots CH \xrightarrow{Cl_2(MeOH)} PhC(OMe)_2{\cdot}CHCl_2$$

The direction in which reaction occurs with unsymmetrical additive reagents doubtless depends on the nature of the substituent groups (R, R′) in the hydrocarbon, but the orientation may, so far as is known, be affected by other factors, *e.g.* the presence of catalysts. Addition can occur to an unsymmetrical acetylene in each of the directions:



$$RC\vdots CR' + XY \rightarrow \begin{cases} RCX:CR'Y \\ RCY:CR'X \end{cases}$$

Thus, in the presence of solutions of mercury salts (*e.g.* mercuric acetate or bromide) or of somewhat diluted sulphuric acid, the acetylenes form addition products (ketones) with water, which frequently consist of a mixture of isomeric compounds:



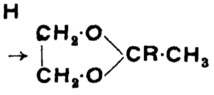
$$RC\vdots CR' \xrightarrow{H_2O} \begin{cases} RC(OH):CHR' \longrightarrow RCO{\cdot}CH_2R' \\ RCH:C(OH)R' \longrightarrow RCH_2{\cdot}COR' \end{cases}$$

Ketones are also reported to be formed when acetylenes are heated with water at 325°.

In the presence of boron trifluoride and mercuric oxide the monoalkyl-acetylenes unite with methyl alcohol and with ethylene glycol to yield ketals: these pass quantitatively into the corresponding ketones on hydrolysis with acids.

$$RC\vdots CH + 2MeOH \rightarrow R{\cdot}C(OMe)_2{\cdot}CH_3$$

$$RC\vdots CH + OH{\cdot}[CH_2]_2{\cdot}OH$$



A similar reaction occurs with monobasic organic acids in presence of small amounts of the same catalysts: in this case mainly mono-addition products (alkenyl esters) are formed, but varying amounts of ketones, probably arising by di-addition, are also formed :

$$\mathrm{RC{:}CH+R'CO_2H \rightarrow RC(O{\cdot}COR'){:}CH_2}$$

$$\mathrm{RC{:}CH+2R'CO_2H \longrightarrow RC(O{\cdot}COR')_2{\cdot}CH_3}$$

$$\mathrm{\xrightarrow{H_2O} RCO{\cdot}CH_3+2R'CO_2H}$$

The acetylenes are absorbed by concentrated sulphuric acid, and in some cases polymerisation to yield aromatic hydrocarbons occurs thereby.

Isomerisation.—According to the early literature acetylenes undergo isomerisation when heated with sodamide, lime, sodium or even alcoholic potash, and rearrangement such as is shown in (A) and (B) below and also the reverse isomerisations are stated to occur.

(A) $\mathrm{RC{:}CMe \rightarrow RCH_2{\cdot}C{:}CH}$

(B) $\mathrm{RC{:}CEt \rightarrow RCH_2{\cdot}CH_2{\cdot}C{:}CH}$

Many of these changes are not well substantiated and it appears probable that some of them are in reality conversions of acetylenes into allenes, since methylacetylene is known to change readily into allene at 550°, and *tert*-butylbenzhydrylacetylene isomerises into *a*-*tert*-butyl-*γγ*-diphenylallene on distillation.

Acetylene.—*See* separate heading.

Methylacetylene, allylene, $\mathrm{CH_3{\cdot}C{:}CH}$, is obtained by the action of alcoholic potash or sodium ethoxide on propylene dibromide, *β*-bromopropylene, *a*- and *β*-chloropropylene, or *ββ*-dichloropropane (Markownikoff, Bull. Soc. chim. 1861, **14**, 90 ; Liebermann, Annalen, 1865, **135**, 267 ; Sawitsch, Compt. rend. 1861, **52**, 399 ; Annalen, 1861, **119**, 186 ; Reboul, Ann. Chim. Phys. 1878 (5), **14**, 463, 477, 481 ; Wislicenus, Langbein, Annalen, 1888, **248**, 326 ; Friedel, *ibid.* 1865, **134**, 262 ; Wislicenus, *ibid.* 1888, **248**, 307). It is formed by the action of water on magnesium methylacetylide obtained by igniting magnesium in acetone vapour (Keiser, Amer. Chem. J. 1896, **18**, 329) ; also to some extent by the action of water on the product obtained by heating magnesium in acetylene, which does not consist entirely of magnesium carbide (Novak, Ber. 1909, **42**, 4209). It may further be obtained from bromomethylacrylic acid or *iso*-bromomethylacrylic acid by boiling with concentrated caustic soda, by distilling their calcium salts, or by electrolysing their potassium salts (Lossen, Annalen, 1905, **342**, 171, 173, 182) ; from potassium or rubidium citraconate or potassium mesaconate by electrolysis (Aarland, J. pr. Chem. 1873 [ii], **7**, 142 ; Hinrich, Schenk, Ber. 1919, **52** [B], 2123) ; in quantitative yield by the action of sodium acetylide on methyl iodide in liquid ammonia (Lebeau, Picon, Compt. rend. 1913, **156**, 1077) ; also by the action of caustic alkali in the cold on tetrolic aldehyde (Claisen, Ber. 1911, **44**, 1166 ; Compt. rend. 1911, **152**, 1491).

Methylacetylene is an unpleasant-smelling gas, which burns with a smoky flame and can be liquefied at 3–4 atm. or by strong cooling. M.p. −110°, b.p. −23·5°. It yields a di- and a tetrabromide with bromine and is reported to yield $\mathrm{CH_3{\cdot}CCl_2{\cdot}CH_3}$ and $\mathrm{CH_3{\cdot}CCl{:}CH_2}$ with hydrogen chloride, $\mathrm{CH_3{\cdot}CBr_2{\cdot}CH_3}$ and $\mathrm{CH_3{\cdot}CBr{:}CH_2}$ with hydrogen bromide, $\mathrm{CH_3{\cdot}CI_2{\cdot}CH_3}$ with hydrogen iodide, and $\mathrm{CH_3{\cdot}CO{\cdot}CHBr_2}$ with hypobromous acid. With strong sulphuric acid in the cold it yields a sulphuric acid compound which is decomposed on treatment with much cold water into acetone and sulphuric acid or, on distilling with a little water, into mesitylene. Since it contains one replaceable hydrogen atom it yields, as does acetylene, numerous metallic derivatives, *e.g.* $\mathrm{C_3H_3Na}$, $\mathrm{C_3H_3Ag}$, $\mathrm{(C_3H_3)_2Hg}$; it reacts with iodine to give *a*-iodomethylacetylene, $\mathrm{C_3H_3I}$, and with ethyl magnesium bromide in ether to yield methylacetylene magnesium bromide,

$$\mathrm{CH_3{\cdot}C{:}CMgBr}$$

For the separation of methylacetylene from acetylene, *see* Berthelot, Ann. Chim. Phys. 1866 [iv], **9**, 423 ; Novak, Ber. 1909, **42**, 4211 ; for the polymerisation of methylacetylene in ultra-violet light, *see* Berthelot, Gaudichon, Compt. rend. 1913, **157**, 138.

Dimethylacetylene, crotonylene, $\mathrm{CH_3{\cdot}C{:}C{\cdot}CH_3}$, is obtained by heating *a*-bromo-Δ^{β}-butene or Δ^{β}-butene dibromide with alcoholic potash or sodium ethoxide under pressure ; also, together with a little ethylacetylene, by the decomposition of calcium carbide with methyl alcohol at 200°. It is a colourless liquid, b.p. 28°. It does not yield metallic derivatives with ammoniacal cuprous chloride, ammoniacal silver nitrate, etc. ; on heating with sodium, however, the sodium derivative of ethylacetylene is formed.

Ethylacetylene, $\mathrm{C_2H_5{\cdot}C{:}CH}$, is obtained by the action of ethyl iodide at −40° on sodium acetylide dissolved in liquid ammonia ; by the action of solid potash on $\mathrm{C_2H_5{\cdot}CCl_2{\cdot}CH_3}$ (from methyl ethyl ketone and $\mathrm{PCl_5}$) ; by the action of alcoholic potash at 100° on $\mathrm{C_2H_5{\cdot}CBr{:}CH_2}$, or by heating Δ^{a}-butene dibromide at 180° with dry caustic potash moistened with a little alcohol. It is a liquid of leek-like odour and sweet taste, m.p. −137°, b.p. 18°, which gives metallic derivatives with ammoniacal cuprous chloride and with silver nitrate solution.

E. H. F.

ACETYL-H-ACID. 1-Acetamino-8-naphthol-3 : 6-disulphonic acid. Intermediate product for the manufacture of dyes.

ACETYLSALICYLIC ACID,

$$\mathrm{AcO{\cdot}C_6H_4{\cdot}CO_2H,}$$

m.p. 134°–135°. *Aspirin*, a valuable analgesic and antipyretic (*v.* Salicylic Acid).

ACHESON GRAPHITE. Lubricants. Suspensions of graphite in water (aqua-dag) or in oil (oil-dag).

ACHIBROMIN Trade name for monobromo*iso*valeryglycolylurea,

$$\mathrm{CH_2(OH)CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_4H_8Br.}$$

ACHILLEA MILLEFOLIUM. *Yarrow. Milfoil.* The blue oil distilled from the flowers contains *l*- and *d*-*a*-pinene, *l*-limonene, *l*-borneol, *l*-camphor, cineol, salicylic acid, and the blue dicyclic hydrocarbon *azulene*, $\mathrm{C_{15}H_{18}}$, b.p. 145°/15 mm., recently named *chamazulene* (Ruzicka and Rudolph, Helv. Chim. Acta, 1926, **9**, 118 ; A. 1926, 299). It is identical with chamazulene from *camomile oil,* and isomeric with the blue hydrocarbons *guaiazulene* and *eucazulene.*

ACHIODIN. Trade name for monoiodo-*iso*valerylglycolylurea,

$$CH_2(OH)CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_4H_8I.$$

ACHRAS SAPOTA. *Chicle.* The dried latex is known as *chicle gum*; it contains the gutta hydrocarbon $(C_5H_8)_n$ together with resin. It is an ingredient of chewing gum.

ACID ALIZARINE BLACKS, BROWNS, BROWN-BLACK, GARNET, GREY, ORANGES, REDS, VIOLET, YELLOW are azo dyes and not derivatives of alizarin.

ACID BLACKS *v.* DYESTUFFS, Azo.

ACID BLUES. Acid Blue B, G, and R are three diphenylnaphthylmethane dyestuffs. Acid Blue EG is a triphenylmethane derivative, and there are five azo dyes termed Acid Blue FRS, GRS, 5RS, SC, and Acid Blue-black.

ACID CHROME BLACKS, BLUES, BROWNS, GREEN, REDS, VIOLET, YELLOW. Azo mordant dyes.

ACID FUCHSINE. Acid magenta. Prepared by sulphonating magenta, and is a mixture of sodium or ammonium salts of the di- and trisulphonic acids (*v.* TRIPHENYLMETHANE DYESTUFFS).

ACID GREENS. Dyes derived from triphenylmethane.

ACID ORANGE *v.* DYESTUFFS, AZO.

ACID VIOLETS include the sulphonic acids of methyl violet (*v.* TRIPHENYLMETHANE DYES).

ACID YELLOWS. Dyes so named occur in the Monazo-, Nitro-, and Pyrazolone classes.

ACIDIMETRY and ALKALIMETRY *v.* CHEMICAL ANALYSIS.

ACIDOL. Trade name for Betaine hydrochloride, $COOH{\cdot}CH_2(NH_3)_3{\cdot}Cl$. Prescribed as a substitute for hydrochloric acid.

ACIDS FROM THE OXIDATION OF PETROLEUM. It is well known that the higher paraffins, *e.g.* paraffin wax, on oxidation in air yield brown products containing saponifiable material. A typical preparation consists in passing air for prolonged periods through melted paraffin wax, the separation of the acids produced by means of the varying solubility of their salts, a subsequent decomposition of the salts and purification of the acid by fractional distillation. Bergmann (Z. angew. Chem. 1918, **31**, 69) obtained by this process an acid of the formula $C_{16}H_{32}O_2$ which he considered to be *iso*palmitic acid.

The velocity of the oxidation process is increased by the application of pressure, and a variety of catalysts has been found of advantage as, for example, compounds of iron, manganese, copper and, in some cases, finely divided metals of the platinum group. Cobalt and manganese naphthenates have been found to be effective catalysts. So large a quantity as 75% of these "wax acids" has been obtained in such an oxidation. Not only the higher acids but also a number of lower acids have been identified in the volatile products obtained, *e.g.* propionic, butyric, valeric, and acids containing 6, 8, and 9 carbon atoms. Furthermore, there is evidence that in the non-volatile portion, myristic, palmitic, and stearic acids as well as *iso*palmitic acid were obtained.

Among other means of assisting the oxidation process may be mentioned the use of nitrogen peroxide, and with this oxidation considerable yields of acetic acid, butyric acid, and the higher acids have been obtained, and similarly the silent discharge and also ozone have been utilised as promoters.

Some interesting and rather important technical developments are due to Burwell (Amer. Chem. Abstr. 1929, **23**, 509), who oxidises liquid hydrocarbons under moderate conditions of temperature and pressure, using as catalysts manganese oleate and manganese stearate. He obtains hydroxylic acids and carboxylic acids ranging from formic up to a group of acids between C_7 and C_{12}, together with a large proportion of oxidation products of high molecular weight.

Ellis (*see, inter alia,* U.S.P. 1516720, 1924) has obtained dibasic acids in the vapour phase oxidation of petroleums with air over a variety of catalysts.

These materials actually have been put forward as blending agents for increasing the lubricating efficiency of straight mineral oils.

For a very comprehensive treatment of this subject special reference should be made to "The Chemistry of Petroleum Derivatives" (Ellis, Chemical Catalog Co., New York, 1934).

A. E. D.

ACIDULIN. Trade name for glutamic acid hydrochloride,

$$COOH{\cdot}[CH_2]_2{\cdot}CH(NH_2)COOH{\cdot}HCl.$$

Used in hydrochloric acid therapy.

ACITRIN. Trade name for ethyl 2-phenylcinchoninate,

$$C_6H_5{\cdot}C_9H_5N{\cdot}COOC_2H_5,$$

m.p. 61°. Used as a remedy for rheumatism.

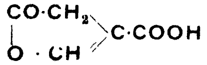
ACOCANTHERA SCHIMPERI (Fam. Apocynaceæ). This African climber contains the poisonous alkaloid *g-strophanthin* or *ouabain*, an arrow poison, which is also prepared from the seeds of *Strophanthus gratus*.

ACOINE. *Guanicaine.* Di-*p*-anisyl-mono-*p*-phenetylguanidine,

$$C_2H_5O{\cdot}C_6H_4{\cdot}N:C(NH{\cdot}C_6H_4{\cdot}OCH_3)_2{\cdot}HCl,$$

m.p. 176°. Local anæsthetic.

ACONIC ACID. *Aci*-formylsuccinic acid lactone, m.p. 164°,



ACONINE *v.* ACONITINE and ACONITE ALKALOIDS.

ACONITIC ACID. An unsaturated tribasic acid,

$$CH_2(COOH){\cdot}C(COOH):CH{\cdot}COOH,$$

contained in *Aconitum napellus*, beetroot, and sugar cane. The *trans*-form has m.p. 194°–195°; the *cis*-, m.p. 125°; the *anhydride*, m.p. 74°.

ACONITINE AND THE ACONITE ALKALOIDS. The numerous species of *Aconitum* which have been examined contain one or more alkaloids of such complexity that their molecular formulæ can only be fixed with great difficulty. Of late years it has been found that various species previously supposed to contain a single alkaloid actually contain several, which further adds to the difficulty of characterising them.

The alkaloids may be arranged in three groups : I. The " aconitines " proper are diacyl esters of polyhydroxy bases (the aconines). They contain a single nitrogen atom ; the aconines contain four methoxy groups ; of the two acids formed on hydrolysis one is always acetic acid, the other may be benzoic, anisic, or veratric, and hence the total number of methoxy groups varies from four to six.

II. Alkaloids containing two nitrogen atoms ; the second one is split off by hydrolysis as anthranilic acid.

III. Alkaloids of much smaller molecular weight than the members of groups I and II, analogous to aconine or acetyl aconine and not yielding an aromatic acid.

Group I.—The best known member is **aconitine**, the chief alkaloid of *Aconitum Napellus L.*, the common monkshood or wolfsbane (*Coqueluchon*, Fr. ; *Eisenhut, Sturmhut*, Ger.) ; it was discovered more than a century ago in the leaves, but is more abundant in the root, which is official (*Aconitum* B.P., U.S.P.) ; it also occurs in *A. Stoerckianum* Reichenb. The alkaloid itself is included in the U.S.P. but no longer in the B.P. It has been chiefly investigated chemically by Dunstan and his pupils (J.C.S. 1891, **59**, 271 ; 1892, **61**, 385, 395 ; 1893, **63**, 994 ; 1894, **65**, 174) and by Majima and collaborators (Ber. 1924, **57** [B], 1466 ; Annalen, 1929, **476**, 203, where see the older literature).

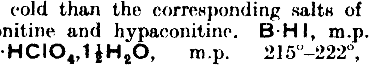
Preparation.—The finely powdered root is exhausted with amyl alcohol mixed with three times its volume of wood spirit. From this extract the wood spirit is distilled under reduced pressure, leaving the whole of the alkaloids dissolved in the residue of amyl alcohol, from which they are removed by agitation with dilute (1%) sulphuric acid. This acid aqueous liquid is shaken with ether to remove ether-soluble, non-basic substances, then made alkaline with dilute ammonia and the liberated alkaloids extracted with ether. The aconine remains dissolved in the water, the aconitine with some benzaconine passing into the ether. The ethereal solution is washed with a small quantity of water and evaporated. The residue is converted into hydrobromide by dissolving it in dilute hydrobromic acid, care being taken to avoid excess of acid. The exactly neutral liquid is evaporated to a small volume and allowed to crystallise. The aconitine hydrobromide is recrystallised until of constant melting-point, and then is converted into the alkaloid by the addition of a slight excess of ammonia to its aqueous solution, the alkaloid being extracted by ether in the usual way. The washed ethereal solution is dried by agitation with fused calcium chloride and evaporated. The small crystals, which are deposited as the ether evaporates, may be recrystallised from dry alcohol by the addition of ether.

Properties.—Colourless, anhydrous, hexagonal prisms of the rhombic system (J.C.S. 1891, **59**, 288 ; Annalen, 1929, **476**, 211, with figure), $C_{34}H_{47}O_{11}N$, m.p. 202°–203°, $[\alpha]_D = +12° 32'$ in alcohol, $+18·7°$ in chloroform. Apt to form mixed crystals with accompanying mesaconitine and hypaconitine (Majima). Easily soluble in chloroform and in benzene, less in alcohol and in ether, very slightly in water, almost insoluble in light petroleum. The aqueous solution is alkaline to litmus.

The salts, in contradistinction to the free base, are lævorotatory. $B{\cdot}HCl,3\frac{1}{2}H_2O$, m.p. 165°–166°, $[\alpha]_D = -31·3°$, crystallises readily from water. $B{\cdot}HBr,2\frac{1}{2}H_2O$ (Dunstan) ; $3\frac{1}{2}H_2O$, m.p. 172°–173° from water, 209°–210° from alcohol-ether (Majima) ; $[\alpha]_D - 30·47°$ (Dunstan), $-27·7°$ (Majima). According to Majima the hydrobromide of aconitine, although readily soluble in hot water, is considerably less soluble in cold than the corresponding salts of mesaconitine and hypaconitine. $B{\cdot}HI$, m.p. 226°. $B{\cdot}HClO_4,1\frac{1}{2}H_2O$, m.p. 215°–222°, $[\alpha]_D -18·9°$. The aurichloride, $B{\cdot}HAuCl_4,1\frac{1}{2}H_2O$, is slightly soluble in water ; it dissolves in less than one part of hot alcohol with $1\frac{1}{2}H_2O$; m.p. 157°–158°.

Reactions.—When aconitine is heated at its melting-point it loses 1 mol. of acetic acid and furnishes a new alkaloid *pyraconitine* and this, on hydrolysis with water or acids, furnishes 1 mol. of benzoic acid and a new base *pyraconine*.

When a salt of aconitine is heated with water, a molecule of acetic acid is split off and the alkaloid *benzaconine*, which also occurs in aconite roots, is formed. Benzaconine in turn, by hydrolysis with alkalis or acids, furnishes 1 mol. of benzoic acid and the alkaloid *aconine*, which is the final basic product of the hydrolysis. Aconitine is therefore acetylbenzoylaconine. Aconitine yields a triacetyl derivative, contains one **NMe** and four **OMe** groups ; it may thus be written,



$$\begin{matrix} CH_3{\cdot}COO \\ C_6H_5{\cdot}COO \end{matrix}\!\!>C_{20}H_{21}NMe<\!\!\begin{matrix} (OH)_3 \\ (OMe)_4 \end{matrix}$$

Oxidation with permanganate yields the neutral substance *oxonitine* (Carr, J.C.S. 1912, **101**, 3241), m.p. 282°, $[\alpha]_D -41·2°$ (Majima), best prepared in acetone + acetic acid solution (Barger and Field, J.C.S. 1915, **107**, 231). The formulæ at first assigned to oxonitine are too small ; the substance is either $C_{31}H_{41}O_{12}N$ (Henry and Sharp, J.C.S. 1931, 581) or more likely

$$C_{32}H_{43}O_{12}N$$

(Späth and Galinovsky, Ber. 1930, **63** [B], 2994), so that only two (or three) carbon atoms are oxidised off ; acetaldehyde is formed in the oxidation (*cf.* Lawson, J.C.S. 1926, 80, and Freudenberg, Ber. 1936, **69** [B], 1962). *Benzaconine*, $C_{32}H_{45}O_{11}N$, prepared as above, is an amorphous dextrorotatory base : $B{\cdot}HCl,2H_2O$, m.p. 215°–216°, $[\alpha]_D -20·7°$. $B{\cdot}HBr,2H_2O$, m.p. 260°–270° (Majima ; *cf.* Freund and Beck, Ber. 1894, **27**, 433, and Schulze, Arch. Pharm. 1906, **244**, 167).

Aconine, $C_{25}H_{41}O_9N$, amorphous and dextrorotatory, is readily soluble in water, alcohol, and chloroform, less so in ether. $B{\cdot}HCl,2H_2O$, prisms, m.p. 169°–170°, $[\alpha]_D^9$ $-3{\cdot}7°$ in water; crystalline tetracetyl derivative, m.p. 241°–242°. For oxidation products of aconine, *see* Schulze (Arch. Pharm. 1908, **246**, 281) and Brady (J.C.S. 1913, **103**, 1621).

Pyraconitine is an amorphous product formed by the loss of acetic acid from aconitine when heated to 190°. Accordingly its formula is $C_{32}H_{43}O_9N$, or H_2O less than the hydrolytic product benzaconine. According to Majima and Suginomé (Ber. 1924, **57** [B], 1471) isomeric *a*- and *β*-varieties are formed (differing in the position of the double bond?). They yield crystalline hydrobromides, aurichlorides and perchlorates.

Detection and estimation.—The identification of aconitine is best accomplished by the determination of the physical constants of its characteristic derivatives but, where minute quantities only are available, the characteristic precipitate given with potassium permanganate (Dunstan and Carr, Pharm. J. 1896 [iv], **2**, 122) and the peculiar tingling sensation produced when even very dilute (1 in 4,000) solutions of aconitine are applied to the tip of the tongue may be utilised, but these reactions are equally applicable to the other alkaloids of group I. The U.S.P., which demands that the root should contain at least 0·5% of aconitine, describes a biological assay of the drug and of aconitine by means of the M.L.D. of 0·00006 mg. per gram of guinea pig; the tincture is adjusted to correspond to 0·15% alkaloid in the drug. For an assay on rats, *see* Munch and Gittinger (J. Amer. Pharm. Assoc. 1929, **18**, 17). Brandt (Arch. exp. Path. Pharm. 1930, **156**, 203) uses the frog's heart and solutions as dilute as 1 per million. It is evident from the above figures that aconitine is an extremely poisonous substance, as are indeed the other alkaloids of groups I and II. With the removal of the acetyl group, the characteristic toxicity is lost in benzaconine. According to Palet (Anal. Asoc. Quím. Argentina, 1918, **6**, 480; Chem. Soc. A. 1920, **118**, ii, 397) aconitine resists putrefaction in the cadaver for two months; in its extraction weak acids and alkalis should be employed, after which it can be identified by physiological tests.

Relation of aconitine to "japaconitine."—After much dispute the identity of the alkaloid from Japanese roots with that of European origin was finally decided by Dunstan and Read (J.C.S. 1900, **77**, 45) and by Makoshi (Arch. Pharm. 1909, **247**, 243), but this problem has been put in a new light by Majima and Morio (Annalen, 1929, **476**, 203), who examined some sixteen Oriental species as well as *A. Napellus*, and conclude that most species contain in addition to aconitine two closely related alkaloids *mesaconitine* and *hypaconitine*. In *A. Napellus* there is something like eight times as much of aconitine as of either of the other two, but in most Oriental species the predominance is reversed and a few contain almost exclusively either mesaconitine or hypaconitine. Whilst the separation of the latter two alkaloids from aconitine is difficult, pure aconitine can be more readily obtained from yet another Japanese species in which it is accompanied only by jesaconitine (*q.v.*). The contradictory results in the European investigations of Japanese roots seem due to imperfect botanical identification and the name japaconitine must be dropped. The approximate content of the four alkaloids in a number of species is tabulated by Majima and Morio and incidentally reveals a variation in total crude alkaloid from 0·14 to 0·76%. Whilst these authors found Merck's crystalline alkaloid (from *A. Napellus*) to contain over 80% of aconitine (the rest being hypaconitine and mesaconitine) the amorphous product of the same firm yielded to Schulze and Berger (Arch. Pharm. 1924, **262**, 553) *neopelline*, amorphous, $C_{28}H_{33}O_5N(OMe)_3,3H_2O$, hydrolysed to *neoline*, $C_{23}H_{39}O_6N$, with a crystalline hydrobromide. It may or may not be identical with hypaconitine or mesaconitine.

Hypaconitine (Majima and Morio, Annalen, 1929, **476**, 171, 203) is practically the only alkaloid in the roots of *A. senanense* Nakai and occurs with small admixtures of aconitine or mesaconitine in several other Japanese species. In a few, and notably in *A. Napellus*, it is much less abundant than aconitine. It has probably the composition $C_{33}H_{45}O_{10}N$ and would then have CH_2O less than aconitine, which it resembles in containing an acetyl, a benzoyl, four methoxy, and one *N*-methyl groups; prisms from methyl alcohol (*Fig.*, *l.c.*, p. 212), m.p. 197°–198°, $[\alpha]_D^{17°}$ $+22{\cdot}7$ in chloroform. The hydrobromide, $B{\cdot}HBr,2\frac{1}{2}H_2O$, m.p. 178°–179°, is more soluble in cold water than that of mesaconitine and much more than that of aconitine; it crystallises from alcohol by adding ether, and is used in the separation of the three alkaloids. The aurichloride, $B{\cdot}HAuCl_4$, has a higher melting-point (243°–245°) than that of mesaconitine (224°–226°) and much higher than that of aconitine (157°–158°). The perchlorate, m.p. 178°–180°, is peculiar in being very soluble in hot alcohol. Oxidation with permanganate furnishes *hypoxonitine*, which may have the formula $C_{31}H_{39}O_{10}N$ and would be analogous to oxonitine except that the oxidation is accompanied by the loss of a molecule of water (the formula assigned by Majima and Morio has to be modified, like the earlier formulæ for oxonitine).

Mesaconitine (Morio, Annalen, 1929, **476**, 181) is the only alkaloid in the root of *A. manschuricum* Nakai (0·7%); predominates largely in some Japanese species and in japaconitine of commerce, but is less abundant than aconitine in other species, and particularly so in *A. Napellus*. It probably has the composition $C_{33}H_{45}O_{11}N$ of a lower homologue of aconitine; it furnishes the same fission products as this alkaloid and the same oxonitine, so that the difference between the two alkaloids must be in the few carbon atoms removed by permanganate. It forms prisms from methyl alcohol, m.p. 208°–209°, $[\alpha]_D^{17°}$ $+25{\cdot}4°$ in chloroform. The hydrobromide, $B{\cdot}HBr,3H_2O$, m.p. 172°–173°, separates from aqueous solution only at high concentrations and can best be crystallised from alcohol. For this and other salts compare hypox-onitine (above).

Indaconitine (Dunstan and Andrews, J.C.S. 1905, **87**, 1620), from *A. chasmanthum*

Stapf. (known in India as "mohri"), crystallises in several forms, and has the composition

$$C_{34}H_{47}O_{10}N,$$

so that it contains one oxygen less than aconitine and appears to be a higher homologue of hypaconitine; m.p. 202°–203°, $[\alpha]_D + 18° 17'$. The hydrobromide, m.p. 183°–187° (anhydrous), $[\alpha]_D - 17° 16'$, crystallises from water in large hexagonal prisms. It contains an acetyl, a benzoyl, and four methoxy groups. *Indaconine*, formed by removal of both acyl groups, is identical with pseudaconine, so that indaconitine only differs from pseudaconitine (*q.v.*) in having a benzoyl instead of a veratroyl group. *Pyroindaconitine* exists in two amorphous forms, yielding different crystalline hydrobromides, of which the α-form has m.p. 194°–198° and the β- m.p. 248°–250°. A second (?) alkaloid from *A. chasmanthum* has been described by Bauer and Radjhan (Pharm. Zentr. 1931, **72**, 145).

Jesaconitine (Makoshi, Arch. Pharm. 1909, **247**, 251; Majima and Morio, Ber. 1924, **57** [B], 1472; Annalen, 1929, **476**, 203) occurs with traces of aconitine in *A. sachalinense* Nakai and with about half as much aconitine in *A. subcuneatum* Nakai (= *A. Fischeri*). It is named after the Japanese northern island Jeso. Although amorphous and yielding an amorphous hydrobromide, it forms a crystalline perchlorate, m.p. 230°–232°, $[\alpha]_D - 16{\cdot}7°$, and aurichloride, m.p. 208°–209°. It has the composition

$$C_{35}H_{49}O_{12}N,$$

and differs from aconitine by the substitution of a *p*-methoxybenzoyl for the benzoyl group; it is acetylanisoylaconine.

Pseudoaconitine (*ψ-aconitine*) (Wright and Luff, J.C.S. 1878, **33**, 151; Mandelin, Arch. Pharm. 1884 [iii], **24**, 97, 129, 161; Henry and Sharp, J.C.S. 1928, 1105; Sharp, *ibid.* 1928, 3095) occurs in *A. deinorrhizum* Stapf. (= *A. ferox* var. *atrox.* Wall), the Nepal aconite of commerce, and also in *A. Balfourii* Stapf. Pseudoaconitine, $C_{36}H_{51}O_{12}N$, has m.p. 214°, $[\alpha]^{20°}_D + 17{\cdot}06°$ in alcohol, $+22{\cdot}75°$ in chloroform. The hydrobromide, m.p. 199°, and the nitrate, m.p. 198°, are most easily crystallised; the hydrochloride is very soluble; the aurichloride, m.p. 235°–236°, may be crystallised from alcohol. The alkaloid contains an acetyl and a veratroyl group and is hydrolysed to pseudoaconine, $C_{20}H_{22}(OH)_4(OMe)_4NMe$, large prisms from acetone containing 1 mol. of solvent, $[\alpha]^{20°}_D + 38{\cdot}7°$ in water, and yielding a tetra-acetyl derivative. The same hydrolytic product is obtained from indaconitine, but no relationship to aconine has been established. Pyro-pseudoaconitine, $C_{34}H_{47}O_{10}N$, forms needles, m.p. 132°–135° (Sharp). Henry and Sharp describe several oxidation products of pseudoaconitine in which the molecule is but slightly altered.

Bikhaconitine (Dunstan and Andrews, J.C.S. 1905, **87**, 1630), from "bikh"-aconite of N.W. India, *A. spicatum* Stapf., $C_{36}H_{51}O_{11}N$, forms button-shaped masses from ether, m.p. 118°–123°, or granules containing $1H_2O$, m.p. 113°–116° from alcohol on addition of water; $[\alpha]^{20°}_D + 12{\cdot}21°$ in alcohol.

$$B{\cdot}HCl,5H_2O,$$

m.p. 159°–161° (anhydrous), $[\alpha]_D - 8{\cdot}86°$ (in water); $B{\cdot}HBr,5H_2O$, m.p. 173°–175° (anhydrous), $[\alpha]_D - 12{\cdot}42°$; $B{\cdot}HI,2\frac{1}{2}H_2O$, m.p. 193°–194° (anhydrous), sparingly soluble in water; $B{\cdot}HAuCl_4$, canary-yellow needles, m.p. 232°–233°. Like pseudoaconitine, bikhaconitine contains an acetyl, a veratroyl, and six methoxyl groups. Veratroylbikhaconine is amorphous but yields a crystalline hydriodide, nitrate, and aurichloride. Bikhaconine, $C_{25}H_{41}O_7N$, also amorphous, yields crystalline salts, and contains one oxygen atom less than pseudoaconine.

All the alkaloids so far mentioned contain a single nitrogen atom and are extremely toxic (Cash and Dunstan, Proc. Roy. Soc. 1902, **68**, 379); pseudoaconitine appears to be much the most toxic. This toxicity is to some extent shared by the alkaloids of group II, containing a second nitrogen atom present as anthranilic acid.

Group II.—Lappaconitine, from the roots of *A. septentrionale* Koelle, is according to Weidemann (Arch. exp. Path. Pharm. 1922, **95**, 166) $C_{32}H_{42}O_9N_2$; prisms, m.p. 223°, $[\alpha]^{18°}_D + 27{\cdot}0°$, hydrolysed by alcoholic potash to acetylanthranilic acid and lappaconine,

$$C_{23}H_{35}O_7N,2H_2O,$$

m.p. 93°, $[\alpha]^{19°}_D + 22{\cdot}4°$, which contains three methoxyl groups. Lappaconitine is highly toxic and is accompanied by the much less toxic **septentrionaline**, $C_{33}H_{46}O_9N_2$, amorphous, containing four methoxyl groups and hydrolysed by alcoholic potash to a base, $C_{25}H_{39}O_7N$, m.p. 89°, $[\alpha]^{25°}_D + 29{\cdot}55°$, and an acid, $C_8H_9O_3N$, m.p. 125°–126°, which when boiled with sodium hydroxide yields anthranilic acid. **Lycaconitine,** $C_{36}H_{46}O_{10}N_2$, **myoctonine,** $C_{36}H_{42}O_{10}N_2$, and an unnamed base were obtained by Schulze and Bierling (Arch. Pharm. 1913, **251**, 8, where see earlier work) from *A. Lycoctonum* L. Lycaconitine is amorphous and is hydrolysed by acids to anthranoyl lycoctonine, leaflets, m.p. 154°–155°, and succinic acid; by sodium hydroxide to lycoctonine, $C_{25}H_{39}O_7N,H_2O$, a strong base crystallising in long needles, m.p. 131°–133°, $[\alpha]^{26°}_D + 49{\cdot}64°$, and succinylanthranilic (lycoctoninic) acid, m.p. 179°. Lycaconitine and myoctonine slowly stop the heart's action.

Group III is composed of little known, comparatively simple alkaloids with a single nitrogen atom and little or no toxicity. **Atisine,** $C_{22}H_{31}O_2N$, from *A. heterophyllum* Wall. of the Himalayas, is the simplest known aconite alkaloid and was last examined by Jowett (J.C.S. 1896, **69**, 1518). It is amorphous, readily soluble in water, alcohol, ether or chloroform, has $[\alpha]^{19°}_D - 19{\cdot}6°$ and furnishes crystalline dextrorotatory salts. Heated with water in a closed tube it gives a hydrate, $C_{22}H_{33}O_3N$. Atisine is non-toxic and *A. heterophyllum* is very commonly used throughout India as a bitter tonic. **Luciduscul**ine, $C_{24}H_{37}O_4N$, was isolated by Majima and Morio (Ber. 1932, **65** [B], 599) from the Japanese *A. lucidusculum* Nakai. Leaflets, m.p. 170°–171°, $[\alpha]_D$ 95·5°. It contains one **NMe** but no **OMe** groups. It is 50,000 times less toxic than aconitine and does not produce a tingling sensation on the tongue. The salts, including a methiodide, are crystalline. The base is hydrolysed by alcoholic potash to acetic acid and *luciculine*, $C_{22}H_{35}O_3N$, a crystalline base yielding a diacetyl derivative and probably related to atisine hydrate.

Palmatine or palmatisine is a crystalline non-toxic alkaloid, m.p. 285°, found in the roots of Indian *A. palmatum D. Don.* (Dunstan and Carr).

Anthorine and **ψ-anthorine** are two ill-defined amorphous alkaloids of low toxicity, observed in *A. Anthora* L. by Goris and Métin (Compt. rend. 1925, **180**, 968).

Paniculatine, $C_{29}H_{35}O_7N$, from *A. paniculatum* Lam., forms rhombic prisms, m.p. 263° (Brunner, Schweiz. Apoth.-Ztg. 1922, **60**, 357); may or may not belong to Group III.

For a detailed account of the aconite alkaloids, *see* F. H. Carr in Allen's "Commercial Organic Analysis," Vol. VII, 5th ed., pp. 227–265.

G. B.

ACOPYRIN *v.* ACETOPYRINE.

ACORIN *v.* ACORUS CALAMUS.

ACORN OIL. Acorn oil has not yet become a commercial article, although in times of oil-shortage it has occasionally been proposed on the Continent to utilise acorns as a domestic source of oil: the residual seed-cake could be employed as a foodstuff for animals. J. L. Baker and Hulton, however, examining acorns from *Quercus robur* containing about 5% of oil, suggest that one of the most obvious applications of acorns is as a source of alcohol (Analyst, 1917, **42**, 351). According to analyses published in the 1926 Rept. of the Connecticut Agricultural Experimental Station (*cf.* Analyst, 1928, **53**, 163) the fresh shelled acorns from white, red, chestnut and scarlet oaks contained 4·1, 15·1, 2·4, and 23·5% of oil respectively at the time of harvesting; somewhat lower oil contents are reported for acorns analysed at the time of germination. Acorn oil is of the non-drying type; an iodine value of 100·7 for the oil from *Quercus agrifolia* is given by Blasdale (J. Amer. Chem. Soc. 1895, **17**, 935), whilst iodine values of 83·0, 90·3, and 81·5 respectively have been reported for the oils from the Indian species *Q. ilex* Linn., *Q. dilatata* Lindl., and *Q. incana* Roxb. (the dried kernels from the last-named tree yielded 16% of oil) by Puntambekar and Krishna (J. Indian Chem. Soc. 1934, **11**, 721).

E. L.

ACORUS CALAMUS (Linn). The common sweet flag, the dried rhizome of which is the drug, an aromatic bitter known as Calamus. Among its constituents are a glucoside *acorin* and an aromatic volatile oil, used in perfumery and for flavouring cordials.

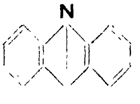
J. N. G.

ACORUS CALAMUS, ESSENTIAL OIL OF. The oil distilled from Acorus Calamus (N.O. *Araceæ*, Linn.) the sweet flag which occurs naturally on the banks of streams, lakes and marshes throughout Europe, Asia and North America. It is cultivated in Burma and Ceylon. All parts are aromatic and contain essential oil, the rhizome yielding up to 0·6% and the dried roots up to 3·5% of oil. The characters of the commercial oil are: sp.gr. 0·958 to 0·970, opt. rot. +9° to +35°, n_D 1·500 to 1·508. Soluble in 90% alcohol. Java oil has sp.gr. 1·077, n_D 1·550. It contains calameone (calamus camphor), m.p. 165°–166°, asarone, m.p. 62°, asaraldehyde, eugenol, heptylic acid esters of acetic and palmitic acids, pinene, camphene, camphor, a sesquiterpene calamene, and a sesquiterpene alcohol calamenenol. It is used in the preparation of liqueurs and for flavouring snuff.

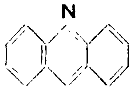
C. T. B.

ACRALDEHYDE *v.* ACROLEIN.

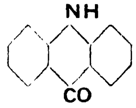
ACRIDINE, $C_{13}H_9N$. This basic substance occurs in crude anthracene from which it may be extracted by dilute acids (Græbe and Caro, Annalen, 1871, **158**, 265). Its representation as 2 : 3–5 : 6-dibenzopyridine accords with its synthesis from diphenylamine, formic acid, and zinc chloride (Bernthsen, Annalen, 1884, **224**, 3), from formyldiphenylamine and zinc chloride and from chloroform and diphenylamine. Confirmation is afforded by its oxidation to 2 . 3-quinolinedicarboxylic acid (acridinic acid) (Graebe and Caro, Ber. 1880, **13**, 100) as well as by its relationship to acridone which is obtained by elimination of water from *o*-phenylaminobenzoic acid. Regarding the arrangement of linkages in the molecule, there are two possibilities. K. v. Auwers and R. Kraul consider that the optical properties favour formula II with seven double linkages (Ber. 1925, **58** [B], 543). In this article, structures I and II are used without prejudice and according to convenience. Acridone (III) may behave tautomerically as 5-hydroxyacridine; it is converted into acridine when distilled with zinc dust. In this article, the numbering system (IV) used in Richter's *Lexikon* will be adopted, though frequent references in the literature are based on scheme V (*see* Thorpe and Linstead, "Synthetic Dyestuffs," Griffin & Co., 7th Ed., 1933, p. 261) and the numbering shown by VI is occasionally found in abstracts of Patent Specifications.



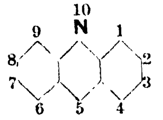
I.



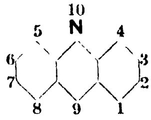
II.



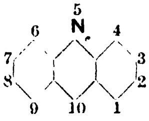
III.



IV.



V.

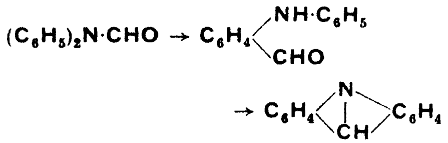


VI.

General Syntheses.—The acridine nucleus may be built up by a variety of reactions.

1. Acridine is formed by heating diphenylamine with formic acid and zinc chloride or formyldiphenylamine with zinc chloride (Bernthsen, Annalen, 1884, **224**, 3). The elimination of water may be preceded by migration of the acyl

group. Formic acid may be replaced by oxalic acid: if acetic or benzoic acids are used



$(C_6H_5)_2N{\cdot}CHO \rightarrow C_6H_4\langle{}^{NH\cdot C_6H_5}_{CHO} \rightarrow C_6H_4\langle{}^{N}_{CH}\rangle C_6H_4$

instead of formic acid, 5-methyl- and 5-phenyl-acridines are formed.

2. Chloroform and diphenylamine yield acridine in the presence of aluminium chloride (O. Fischer and G. Körner, Ber. 1884, **17**, 101).

3. Passage of phenyl-*o*-toluidine through a red-hot tube gives acridine (Graebe, Ber. 1884, **17**, 1370).

4. Acridine is formed by distillation of *o*-aminodiphenylmethane over lead oxide (O. Fischer and H. Schütte, Ber. 1893, **26**, 3086).

5. Small amounts of acridine are produced by heating benzaldehyde with aniline to 260° (R. Möhlau, Ber. 1886, **19**, 2452); or by the action of phosphorus pentoxide on salicylaldehyde-anil (F. Blau, Monatsh. 1897, **18**, 681).

6. A good yield of acridine is said to be given by passing benzylaniline vapour through a red-hot tube (H. Meyer and A. Hofmann, Monatsh. 1916, **37**, 681).

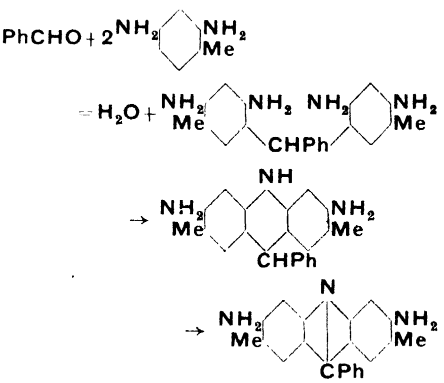
7. Acridine is formed in the reduction of *o*-nitrodiphenylmethane (O. Fischer, Ber. 1895, **28**, 1335). A. Kliegl (Ber. 1909, **42**, 591; *cf.* E. Bamberger, *ibid.* 1721) obtained acridone by heating *o*-nitrodiphenylmethane, he considered that phenylanthroxan (*iso*-benzoxazole) was an intermediate product and confirmed this view by directly heating phenylanthroxan. Small amounts are also produced in the preparation of *o*-nitrodiphenylmethane from *o*-nitrobenzyl chloride, benzene, and aluminium chloride.

8. Acridones are formed by dehydration of arylanthranlic acids with concentrated sulphuric acid (Jourdan, Ber. 1885, **18**, 1447; Graebe and K. Lagodzinski, Ber. 1892, **25**, 1733; Annalen, 1893, **276**, 47; M. Schöpf, Ber. 1892, **25**, 1981). K. Matsumwra (J. Amer. Chem. Soc. 1935, **57**, 1533) finds that much acridone-2-sulphonic acid (and some 4-acid) is produced at 80°. According to M. Polaczek (Rocz. Chem. 1935, **15**, 565) acridone is sulphonated in position 3 at 100°.

9. Condensation of *o*-nitrobenzaldehyde with aromatic hydrocarbons by concentrated sulphuric acid containing a small amount of sodium nitrite gives acridones (K. Lehmstedt, Ber. 1932, **65** [B], 834). Compare papers by I. Tănăsescu and co-workers (Bull. Soc. chim. 1931 [iv], **49**, 1295; 1933 [iv], **53**, 372, 381, 918; 1934 [v], **1**, 547).

10. Reduction of 2 : 4 : 2′ : 4′-tetranitrobenzophenone with stannous chloride and hydrochloric acid gives 2 : 8-diaminoacridone directly (Schöpf, Ber. 1894, **27**, 2318); reduction of 2 : 2′-dinitrobenzophenone gives the corresponding diamino-compound convertible into acridone by heating with concentrated hydrochloric acid or zinc chloride (W. Staedel, Ber. 1894, **27**, 3362).

11. Many acridine dyestuffs have been produced by condensation of an aldehyde with two molecules of a metadiamine, elimination of ammonia and oxidation of the resultant dihydroacridine. This oxidation is often carried out with ferric chloride, *e.g.*:

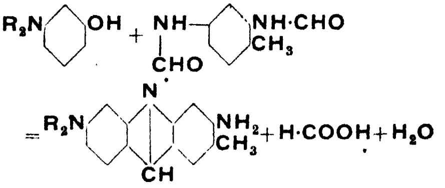


A similar reaction can be effected starting with aminocresol ($CH_3 : OH : NH_2 = 1 : 2 : 4$) and formaldehyde and resulting in dihydroxydimethylacridine (Cassella & Co., G.P. 120466, 1900. *See further* F. H. Kranz and Nat. Aniline and Chem. Co. Inc., U.S.P. 1986111).

12. Condensation of *p*-aminobenzaldehyde with *m*-aminodiphenylamine or its homologues yields derivatives of dihydroacridine which may be oxidised to the corresponding acridine (B.A.S.F., G.P. 102072, 1897). *p*-Aminobenzylideneaniline has also been employed; in both cases phosphine dyes are the end products.

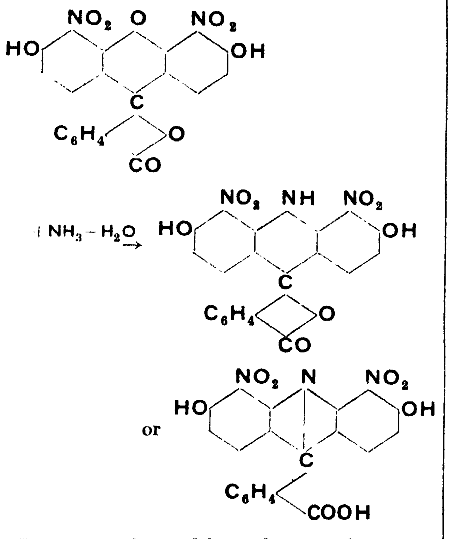
13. Formaldehyde can be condensed with two molecules of *m*-toluylenediamine or two molecules of *β*-naphthol to give tetraminoditolylmethane or dihydroxydinaphthylmethane respectively. If the former (latter) is heated with *β*-naphthol (*m*-toluylenediamine), one molecule of *m*-toluylenediamine (*β*-naphthol) is eliminated and an aminomethylphenonaphthacridine results (F. Ullmann and E. Naef, Ber. 1900, **33**, 912; G.P. 104748, 1898; *cf.* P. Julius and W. Reese, U.S.P. 644324, 1899).

14. Diformyldiamines have been condensed with dialkyl-*m*-aminophenols to yield acridines (J. R. Geigy, G.P. 161699, 1903).



15. Prolonged heating of fluorescein with ammonia under pressure gives 2 : 8-diamino-5-*o*-carboxyphenylacridine (R. Meyer, Ber. 1888, **21**, 3376). Pyrone oxygen is replaced by NH when ammonia reacts with 4 : 5-dinitro-

fluorescein in the cold (F. Reverdin, Ber. 1897, **30**, 332).



The yields obtained from these synthetic processes are often indifferent. Since acridones are easily accessible, methods depending on the reduction of these compounds are useful. British Dyestuffs Corp., Ltd., and W. H. Perkin (B.P. 214756, 1923) prepare acridine in the following manner: Acridone (4 parts) is reduced in presence of sodium carbonate (23 parts) and 95% alcohol (121 parts) by 4% sodium amalgam (240 parts), the reaction being carried out in presence of carbon dioxide. Temperature for the first hour is 75°, for the second 80°, and finally the mixture is heated for 3 hours at 80°-85°. Alcohol is distilled off, water added, and the precipitated dihydroacridine purified by crystallisation from alcohol. Oxidation of the dihydroacridine gives acridine. It is stated that a nitroacridone reduces to an aminodihydroacridine; before oxidising the latter, it must be protected by acetylation. I.G. Farbenind. (B.P. 367024, 367037) state, however, that "3-nitroacridone" is reduced to the "3-aminoacridone" prepared by Grandmougin (Ber. 1913, **46**, 3432). 2-Nitroacridone (Richter numbering) is actually referred to.

Isolation from coal-tar.—Graebe and Caro extracted acridine from the fraction of coal-tar boiling at 300°–360° by dilute sulphuric acid, precipitated with potassium dichromate, recrystallised the acridine chromate from hot water, basified with ammonia, dissolved the acridine in hot dilute hydrochloric acid and decomposed the acridine hydrochloride with ammonia (Annalen, 1871, **158**, 265; Ber. 1880, **13**, 99).

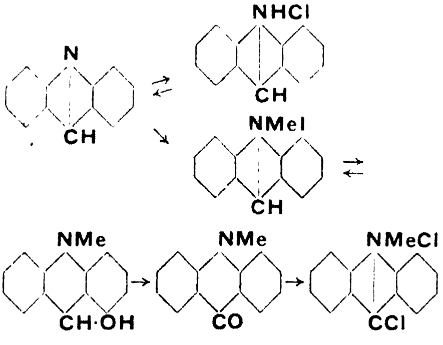
E. Wirth (440771, 1925) recovers acridine from "anthracene-oil" after removal of phenolic substances by caustic soda by conversion into the addition product with sodium bisulphite and decomposition of the salt by caustic soda. 1,000 kg. of the oil are vigorously agitated with 2 kg. sodium bisulphite and 4 litres water. The sulphonate separates and on decomposition with caustic soda yields about 2·8 kg. acridine of about 90% purity.

Properties.—Acridine forms small colourless needles or four-sided rhombic prisms, m.p. 111°, b.p. above 360°. F.P. const., Δ=12·0: P. Pfeiffer and H. Pfitzner, J. pr. Chem. 1936 [ii], **145**, 246, 255. It sublimes appreciably at 100° and is volatile with steam. Sparingly soluble in hot water, easily in alcohol, ether and carbon disulphide; the solutions show a blue fluorescence. Exposed to sunlight, acridine forms pale yellow crystals, m.p. 276° (Orndorff and Cannon, Amer. Chem. J. 1895, **17**, 558). Absorption spectrum (D. Rădulescu and G. Ostrogovich, Ber. 1931, **64** [B], 2233. Further references regarding derivatives given later). It induces violent sneezing when inhaled as dust or vapour, in solution both the base and its salts cause considerable skin irritation.

GENERAL REACTIONS.

1. As tertiary bases, acridine and its derivatives form salts with acids and yield quaternary acridinium salts with methyl iodide, sulphate, etc. Action of alkalis regenerates acridine from the salts.

2. The quaternary acridinium salts give carbinol (pseudo-) bases which, if the 5-hydrogen atom is unsubstituted, are easily oxidised to N-substituted acridones. The constitution of these pseudo-bases was first recognised by A. Hantzsch and M. Kalb (Ber. 1899, **32**, 3121). They also found that 10-methyl-5-phenylacridinium salts give a colourless, crystalline cyanide, m.p. 176°, corresponding in structure to the carbinol base. 10-alkylacridones are converted into 5-chloro-10-alkylacridinium chlorides by the action of phosphorus pentachloride and similar compounds.



3. In the case of amino-acridines, 10-alkylacridinium salts may be obtained by acetylating the amino-groups, acting on the acetaminoacridine with alkyl iodide, sulphate, etc., and subsequently removing the acetyl groups by acid hydrolysis (*see* ACRIFLAVINE).

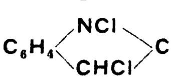
4. Oxidation of acridine gives quinoline-2 : 3-dicarboxylic acid.

5. Reduction gives 5 : 10-dihydro derivatives; these may be reoxidised to the original acridines. Reduction to dihydroacridine has been effected by hydrochloric acid and zinc dust as well as by sodium amalgam (Bernthsen and Bender,

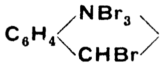
Ber. 1883, **16**, 1972, 2831). Heated with hydrogen in presence of finely divided nickel, 2 : 3-dimethylquinoline is formed (Padoa and Fabris, Atti R. Accad. Lincei, 1907 [v], **16**, i, 921).

6. Nitric acid gives substitution products. Thus Graebe and Caro (Annalen, 1871, **158**, 275) obtained two (m.p. 154° and 214°) mono-acridines and one di-nitro- by the action of nitric acid ; A. E. Dunstan and R. O'F. Oakley chlorinated 5-phenylacridine (Ber. 1906, **39**, 981) which Bernthsen had previously dinitrated and disulphonated (Annalen, 1884, **224**, 29, 32). The orientation of the substituent groups has been determined, by Jenson and Friedrich, J. Amer. Chem. Soc. 1927, **49**, 1049, and Secareanu, Ber. 1931, **64** [B], 837 as the 1-, 3-, and 1 : 3-derivatives respectively.

7. Direct action of halogens on acridine gives addition compounds such as :



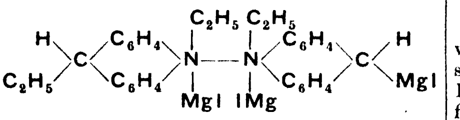
m.p. 240° ;



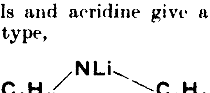
m.p. 220°, decomp.

(Senier and Austin, J.C.S. 1904, **85**, 1196). Heating with flowers of sulphur produces thio-acridone. Sodium bisulphite adds on in the 5 : 10-position ; the SO_3Na group attached at 5 may be replaced by the cyanogen radical giving an acridan-nitrile. 5-Cyanodihydroacridine, m.p. 146°, formed from sodium acridan-sulphonate, oxidises in air to 5-cyanoacridine, m.p. 186° (Wirth, G.P. 440772, 1925), and this may be used as a source of acridine-5-carboxylamide, m.p. 263°–264°, and acridine-5-carboxylic acid, m.p. 289°–290° (decomp.). *See further*, K. Lehmstedt and E. Wirth, Ber. 1928, **61** [B], 2044.

8. Alkyl iodomagnesium compounds of acridine were obtained by Senier, Austin, and Clarke (J.C.S. 1905, **87**, 1469), who regard them as derivatives of NN′-dihydrodiacridyl, *e.g.* :



Lithium aryls and acridine give addition products of the type,



which are decomposed by water giving 5-aryl-5 : 10-dihydroacridines. The action of lithium aryls on N-methylacridone was also examined (E. Bergmann, O. Blum-Bergmann, and A. F. von Christiani, Annalen, 1930, **483**, 80).

Salts.—The *hydrochloride*, $B{\cdot}HCl,H_2O$, is colourless and easily soluble in water, the *mercuri-*, *platini-* and *auri-chlorides* are insoluble or sparingly so. The *nitrate* is difficultly soluble in cold water and the *chromate* and *picrate* are difficultly soluble, even in hot water.

Acridine combines with alkyl iodides and sulphates giving coloured quaternary ammonium compounds. The *methiodide* splits up smoothly into acridine and methyl iodide when heated (Decker and Dunant, Ber. 1906, **39**, 2721). On treating their solutions with alkalies, colourless precipitates, soluble in organic solvents are obtained. The pseudo-base (carbinol) precipitated from acridine methiodide yields non-volatile methylacridone and volatile N-methyldihydroacridine on steam distillation (Pictet and Patry, Ber. 1902, **35**, 2536). Confirmatory evidence of the relationships existing between the alkyl-acridinium compounds, their pseudo-bases, and the acridones is afforded by their absorption spectra (C. K. Tinkler, J.C.S. 1906, **89**, 858 ; *cf. also* Dobbie, Lauder, and Tinkler, J.C.S. 1903, **83**, 598, and Dobbie and Tinkler, J.C.S. 1904, **85**, 1005 ; 1905, **87**, 269).

Alkyl- and Aryl-acridines and their Derivatives.—3-*Methylacridine*, m.p. 131·5°. Prepared by heating phenyldiaminoditolylmethane with zinc dust (Ullmann, J. pr. Chem. 1887 [ii], **36**, 265).

$$C_6H_5{\cdot}CH[C_6H_3(CH_3)(NH_2)]_2$$
$$= 1:4\text{-}C_6H_4(CH_3)(NH_2)+C_{13}H_8(CH_3)N$$
$$+H_2$$

5-*Methylacridine.*—Formed as a by-product when acetonitrile and diphenylamine hydrochloride are heated to 220°. 56% of the theoretical amount is obtained by heating 50 g. diphenylamine, 30 c.c. glacial acetic acid, and 85 g. zinc chloride for 14 hours at 220° (Bernthsen, Annalen, 1884, **224**, 35); m.p. 114° (Bernthsen), 92°–94° (E. Besthorn and O. Fischer, Ber. 1882, **15**, 1500 ; 1883, **16**, 74). O. Blum gives 117°–118° and states that the substance melting at 90°–100° is an addition product of 5-methylacridine and diphenylamine (Ber. 1929, **62** [B], 881). *Methiodide*, red needles, m.p. 263°, decomp. ; *carbinol base*, small white crystals.

The methyl group in 5-methylacridine is reactive, thus it gives methylacridinechloral,

$$C_{13}H_8(CH_2{\cdot}CH(OH)CCl_3)N,$$

when warmed with anhydrous chloral in benzene solution (Bernthsen and Mulhert, Ber. 1887, **20**, 1543). L. Monti (Gazzetta, 1933, **63**, 721) finds that formaldehyde and secondary bases (dimethylamine and piperidine) react to give compounds with the grouping :

$$(C_{13}H_8N){\cdot}CH_2{\cdot}CH_2{\cdot}NRR'$$

F. M. Hamer (J.C.S. 1930, 997) has condensed the methiodide with 2-iodoquinoline methiodide and ethiodide, the resulting dyes,

$$MeN(C_6H_4)_2C:CH{\cdot}C_9H_6{\cdot}N(RI),$$

are devoid of sensitising properties.

Other 5-*alkylacridines* were prepared by Bernthsen.

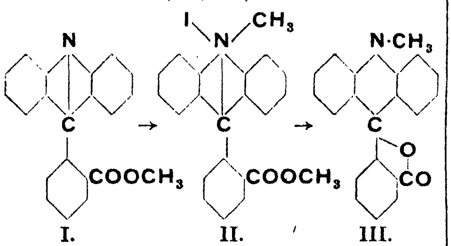
5-*Phenylacridine.*—Prepared by heating benzonitrile with diphenylamine to 230°–250° (Bernthsen, Annalen, 1878, **192**, 19) ; by heating benzoyldiphenylamine with zinc chloride (Annalen, 1884, **224**, 12) or by heating 50 g. benzoic acid, 70 g. diphenylamine, and 150 g.

zinc chloride for 10 hours at 160°. For purification, *see* Dunstan and Oakley (Ber. 1906, **39**, 977). M.p. 181°, b.p. 403°–405° (uncorr.). Halogenation gives *dichloro-* and *tribromo*-derivatives. Energetic nitration gives a *trinitro*-derivative ; by regulated nitration, Dunstan and Oakley obtained a *dinitro*-compound and assumed that the nitro-groups entered positions 2 and 8. 5-p-*Chlorophenylacridine* (Dunstan and Hilditch, J.C.S. 1907, **91**, 1661) ; 5-p-*bromophenylacridine*, m.p. 234° (uncorr.) (Dunstan and Stubbs, Ber. 1906, **39**, 2402). Bernthsen obtained a *disulphonic* acid from phenylacridine which he isolated as the sodium salt (*l.c.* 32).

5-*Phenyl-10-alkylacridinium compounds*.—Methyl iodide acts on phenylacridine at 70°–100° (Bernthsen, *l.c.* 29) ; Decker employed methyl sulphate (Ber. 1905, **38**, 1148). It is also formed by the action of phenyl-magnesium bromide on *N*-methylacridone. The carbinol pseudo-base, m.p. 108°, was examined crystallographically by Bernthsen and Osann (Ber. 1886, **19**, 427).

3-*Methyl-5-phenylacridine*.—M.p. 135°–136° (Bernthsen, Annalen, 1887, **239**, 60). Gives 5-phenylacridine-3-carboxylic acid on oxidation with chromic acid.

5-*o-Carboxyphenylacridine*.—(Acridylbenzoic acid, diphenylaminephthalein.) Obtained by heating 30 g. phthalic anhydride, 45 g. diphenylamine and 75 g. zinc chloride for 10–14 hours at 180°–200° (Bernthsen, Annalen, 1884, **224**, 45). It forms yellow needles, m.p. 347° ; almost insoluble in boiling water, sparingly soluble in organic solvents. It functions both as an acid and a base; solutions in acids show green fluorescence; alkaline solutions give a beautiful blue fluorescence on strong dilution. Methyl iodide gives the hydriodide of the methyl ester, the free ester (I) bright yellow needles, m.p. 173°, adds methyl sulphate to form an acridinium salt from the solution of which potassium iodide precipitates the methiodide, (II) red needles, m.p. 226°–227°. Addition of caustic soda to solutions of these salts causes gradual precipitation of the lactone (III), colourless leaflets, m.p. 245°. It is assumed that a betaine is formed intermediately (Decker and Hock, Ber. 1904, **37**, 1002 ; Decker and Schenk, Ber. 1906, **39**, 748).

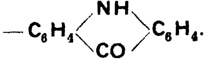


I. II. III.

Other methods by which derivatives of this compound are formed are to be found under *General Syntheses* (15) (page 126) and *Flaveosine* (page 133).

Hydroacridines.—As already mentioned, 5 : 10-dihydroacridine is obtained from acridine by reduction with sodium amalgam or zinc and hydrochloric acid. Graebe (Ber. 1883, **16**, 2831) also obtained octahydroacridine, m.p. 48°, b.p. 320°, by reduction with hydriodic acid and amorphous phosphorus at 220°–230°. W. H. Perkin and W. G. Sedgwick (J.C.S. 1924, **125**, 2457 ; 1926, 438) examined tetra- and octahydroacridines and obtained the latter in two forms : A, m.p. 82°, and B, m.p. 72°. Each of these was optically inactive but capable of resolution giving for A, m.p. 85° and $[\alpha]_D$ +33° ; for B, m.p. 73° and $[\alpha]_D$ ±23°.

Acridone.—

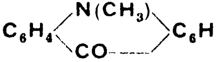


$C_6H_4\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle C_6H_4$. Prepared by warming phenylanthranilic acid with concentrated sulphuric acid. Thick yellow needles, melting above 350° and volatile without decomposition. Fairly soluble in hot alcohol and boiling acetic acid with yellow colour and blue fluorescence. Soluble in hot hydrochloric acid, crystallising out on cooling, insoluble in aqueous alkalis. Yields acridine on distillation with zinc dust (C. Graebe and K. Lagodzinski, Ber. 1892, **25**, 1734 ; *cf.* B.P. 214756). Ullmann and co-workers (Annalen, 1907, **355**, 312) later improved the method for making arylanthranilic acids and described a number of derivatives of acridone. Lehmstedt and Hundertmark prepared acridone by the action of sodium hypochlorite on thioacridone (Ber. 1931, **64** [B], 2381. They studied the nitration in detail).

Acridones are obtained by hydrolysis of *s*-chloroacridines by boiling with dilute hydrochloric acid (N. S. Drozdov and N. S. Leznova, J. Gen. Chem. Russ. 1935, **5**, 690, 1576, 1736).

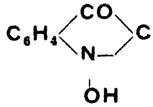
For other references, *see General Syntheses*

5-*Methylacridone*.—

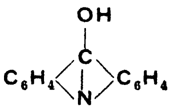


$C_6H_4\left\langle\begin{matrix}N(CH_3)\\CO\end{matrix}\right\rangle C_6H_4$, m.p. 191°. From acridine methiodide and alkali, the —CH·OH group of the carbinol base oxidises in the air (H. Decker, J. pr. Chem. 1892 (ii), **45**, 194). Lehmstedt and Hundertmark (Ber. 1931, **64** [B], 2286) oxidise with chromic acid and give m.p. 199°. The compound nitrates in 3 or 3 : 7 positions, the dinitro-derivative was used as an intermediate in the synthesis of 3 : 7-diamino-10-methylacridinium chloride (isomeride of acriflavine). Reduction may lead to salts of 10 : 10′-dimethyl-5 : 5′-diacridinium or of 10-methyl-5-acridinium or to 10-methyl-dihydroacridine itself.

A. Kliegl and A. Fehrle (Ber. 1914, **47**, 1629) obtained phenylanthranil on condensing *o*-nitrobenzaldehyde with benzene but this was accompanied by a yellow substance, $C_{13}H_9O_2N$, which they assumed to be 10- (*N*-) hydroxyacridone (I) since on mild reduction it gave acridine and a base isomeric with acridone. The latter was supposed to be 5-acridol (II).



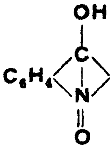
I.



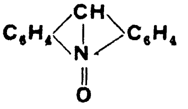
II.

I. Tănăsescu and E. Ramontianu regard these compounds as 5-hydroxyacridine-*N*-oxide

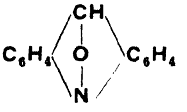
(III), and acridine-*N*-oxide (IV) respectively (Bull. Soc. chim. 1934 (v), **1**, 547).



III.



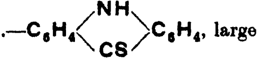
IV.



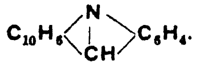
V.

K. Lehmstedt (Ber. 1935, **68** [B], 1455) held the same view with regard to the condensation product but considered the base formed by reduction with sodium amalgam to have the constitution (V). Later he modified his views (Ber. 1936, **69**, [B], 1155). A compound produced by the action of benzoic peracid on acridine in benzene solution is isomeric with I and III, and is regarded as *acridine*-5 : 10-peroxide by Lehmstedt and Klee (*ibid.* 1514). A. Kliegl and A. Brösamle look on formulæ I and III as tautomeric (*ibid.* 197); Tănăsescu and Ramontianu consider there is no tautomerism in the case of 5-hydroxyacridine-*N*-oxide, to which they assign an orthoquinonoid instead of a bridged ring structure (*cf.* III). It can be obtained by hydrolysis of 5-chloroacridine-*N*-oxide, and gives the same absorption spectrum in alcoholic and alkaline solutions (*ibid.* 1825). Several earlier papers both by Lehmstedt (Ber. 1932, **65**, [B], 834, 999) and Tănăsescu (Bull. Soc. chim. 1927 [iv], **41**, 528, 1497, 1511; 1928, [iv], **43**, 1117, 1264; 1931 [iv], **49**, 1295) deal with syntheses of acridones and various compounds are described.

The reactivity of groups in substituted acridones (*e.g.* 1-chloro-4-nitro-, m.p. 320° ; 1-bromo-4-nitro-, m.p. 325°) has been studied by H. B. Nisbet (J.C.S. 1932, 2772 ; 1933, 1372). K. Matsumara (J. Amer. Chem. Soc. 1929, **51**, 816) has described 2 : 8-dihydroxy- and dimethoxy-acridones and N. S. Drozdov and S. S. Drozdov (J. Gen. Chem. Russ. 1934, **4**, 1) have condensed substituted diphenylamine-carboxylic acids with phosphoryl chloride. Acridone-3-arsonic (and stibonic) acids have been prepared by M. M. Barnett, A. H. C. P. Gillieson, and W. O. Kermack (J.C.S. 1934, 434).

Thioacridone.— $C_6H_4\overset{NH}{\underset{CS}{\langle\rangle}}C_6H_4$, large red needles, m.p. 275°, is obtained by melting acridine with sulphur or by heating acridone with sulphur and phosphorus to 260°. The alkaline solutions contain the tautomeric thiol form and may be benzylated and benzoylated. With phosphorus pentachloride it gives 5-chloroacridine, and with phosphorus and bromine 5-bromoacridine, m.p. 119°, from which iodoacridine, m.p. 169°, may be obtained by treatment with alcoholic potassium iodide (A. Edinger, Ber. 1900, **33**, 3769; M. Polaczek, Rocz. Chem. 1936, **16**, 76).

Phenonaphthacridines.—



$C_{10}H_6\overset{N}{\underset{CH}{\langle\rangle}}C_6H_4.$

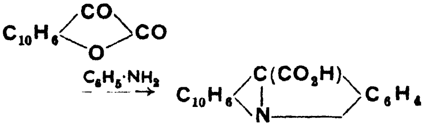
Two compounds are known in which the nitrogen atom occupies the α or the β position with regard to the naphthalene nucleus.

α-*Phenonaphthacridine*, m.p. 108°, was prepared by F. Ullmann and A. La Torre (Ber. 1904, **37**, 2924) by heating *o*-tolyl-1-naphthylamine with lead oxide. The compound had been previously obtained by A. Pictet and S. Ehrlich (Annalen, 1891, **266**, 155), who described it as α-chrysidine.

β-*Phenonaphthacridine*, m.p. 131°, was first described as β-chrysidine (P. and E.), its constitution was recognised and various syntheses effected by Ullmann and his co-workers (Ber. 1900, **33**, 910 ; 1902, **35**, 2670 ; 1904, **37**, 2922, 2926). Another synthesis is given by J. Martinet and A. Dansette (Bull. Soc. chim. 1929 [iv], **45**, 101). *N*-Phenyl-β-naphthylamine and ethyl mesoxalate are condensed to ethyl 1-phenyl-4 : 5-benzodioxindol-3-carboxylate, which on treatment with 10% caustic potash yields phenonaphthacridine carboxylic acid. This loses carbon dioxide on heating. Numerous amino- derivatives of the compound have been patented, they have been mostly obtained using β-naphthylamine, an arylene-diamine, and an aldehyde as initial material. (For patent literature, *see* Hewitt, "Dyestuffs derived from Pyridine, Quinoline, Acridine and Xanthene," Longmans, Green and Co., 1922, pp. 195–205).

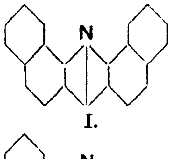
Phenonaphthacridones *see* Ullmann and Rasetti, Annalen, 1907, **355**, 351.

A synthesis which may lead to phenonaphthacridines or to naphthacridines is due to K. Fries (I.G. Farbenind. A.-G., G.P. 446543, 1926). β-Naphthocoumarandione is heated with a primary arylamine in acid solution, *e.g.* :

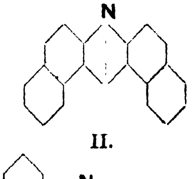


The products are decarboxylated when heated above their melting points. Examples are given of the use of *p*-anisidine, *p*-amino-acetanilide and β-naphthylamine.

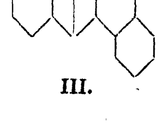
Naphthacridines.—Four of these isomeric compounds have been prepared; they may be represented by the following structures :—



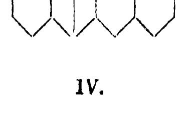
I.



II.



III.



IV.

I. α-*Naphthacridine*, pale yellow crystals, m.p. 173°, prepared by melting together α-naphthylamine, methylene iodide and potassium carbonate (A. Senier and W. Goodwin, J.C.S. 1902, **81**, 288). A disulphonic acid derivative is obtained from naphthionic acid and formaldehyde (R. Möhlau and O. Haase, Ber. 1902, **35**, 4175).

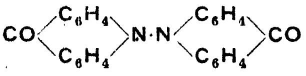
II. β-*Naphthacridine*, yellow prisms, m.p. 216°, first prepared by Reed (J. pr. Chem. 1886 [ii], **35**, 314) by the action of methylal (with or without acetone) on β-naphthylamine in presence of hydrogen chloride. G. T. Morgan (J.C.S. 1898, **73**, 541) substituted formaldehyde for the methylal and obtained β-naphthacridine in admixture with *iso*naphthacridine (orange-coloured needles, m.p. 225°–226°) and a base (colourless prisms, m.p. 202°–203°). Each of the last two compounds is convertible into naphthacridine. Senier and Goodwin (*l.c.* 289) employed methylene iodide. Ullmann and Fetvadjian (Ber. 1903, **36**, 1027) heated together a mixture of β-naphthylamine, β-naphthol, and trioxymethylene. A disulphonic acid derivative is obtained from 2-naphthylamine-6-sulphonic acid and formaldehyde (Möhlau and Haase, *l.c.* 4173).

III. Pale yellow needles or leaflets, m.p. 228°. from α-naphthylamine and dihydroxydinaphthylmethane (product of formaldehyde and β-naphthol) at 200°, or from α-naphthylamine β-naphthol and trioxymethylene or from methylene-α-naphthylamine and β-naphthol (Ullmann and Fetvadjian, *l.c.* 1029).

IV. Small yellow needles, m.p. 205·5°–206°. The corresponding naphthacridone (yellow needles or leaflets) is obtained by heating 2-hydroxy-3-naphthoic acid with β-naphthylamine, b.p. 260°–280° ; the acridone gives the acridine on distillation with zinc dust (E. Strohbach, Ber. 1901, **34**, 4146).

A number of vat-dyestuffs are known in which one benzene ring of an acridone nucleus is also common to an anthraquinone or similar nucleus (*see* Vat Dyestuffs).

Diacridines.—Linking between two acridine residues can take place through the meso-carbon atoms. Linking of the two nitrogen atoms seems improbable, but Graebe and Lagodzinski (Annalen, 1893, **276**, 35) assumed that *bisacridonyl*, m.p. 251°, formed by the oxidation of acridone, possessed the structure :

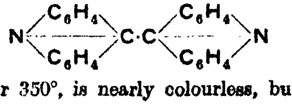


$$\mathrm{CO}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{N{\cdot}N}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{CO}$$

Its solutions are non-fluorescent, it is insoluble in alcoholic alkalis and forms acridine on heating with zinc dust. Oxidation of methylacridone to bisacridonyl is difficult.

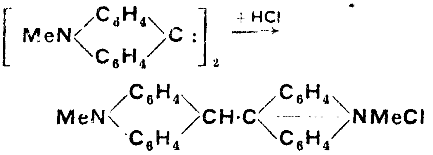
Formulæ involving linkage between the nitrogen atoms were adopted by Senier, Austin, and Clarke, and by Lehmstedt and Hundertmark in certain cases (Ber. 1929, **62** [B], 414).

5 : 5-*Diacridyl*.—



$$\mathrm{N}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{C{\cdot}C}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{N}$$

m.p. over 350°, is nearly colourless, but gives yellow salts. It is produced by the action of copper powder on 5-chloroacridine at 140°, or on thioacridone at 280° in an atmosphere of carbon dioxide (Lehmstedt and Hundertmark, Ber. 1929, **62** [B], 1065 ; 1930, **63** [B], 1229 ; *cf.* E. Bergmann and O. Blum-Bergmann, *ibid.* 757). Diacridyl was first obtained by Decker and Dunant (Ber. 1909, **42**, 1176) by elimination of methyl iodide from acridine methiodide. Reduction of methylacridone with zinc dust and acetic acid gives a mixture of substances from which diacridyl dimethonitrate may be isolated, from this salt the methiodide is obtained by the action of potassium iodide. The corresponding di-carbinol pseudo-base was isolated by Lehmstedt and Hundertmark. K. Gleu and W. Petsch (Angew. Chem. 1935, **48**, 57) found that if hydrogen peroxide is added to a freshly prepared alkaline solution a green chemiluminescence is obtained similar in colour to the fluorescence of the methonitrate. H. Decker and W. Petsch (J. pr. Chem. 1935 [ii], **143**, 211) have further examined the chemiluminescent reactions of NN′-dimethyldiacridylium (*luzigenin*) salts. Reduction gives dimethyldiacridine, m.p. 385°, decomp. 290°,



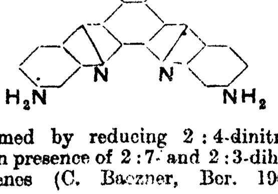
$$\left[\mathrm{MeN}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{C:}\right]_2 \xrightarrow{+\,HCl}$$

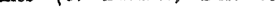
$$\mathrm{MeN}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{CH{\cdot}C}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle\mathrm{NMeCl}$$

which forms methylacridan-acridinium methochloride. Oxidation of the latter gives a salt of *luzigenin*, the reaction being accompanied by chemiluminescence.

The reduction of 2 : 8-diamino-10-methylacridone by sodium amalgam in methyl alcoholic solution followed by oxidation with ferric chloride in hydrochloric acid solution leads to the formation of *tetramino-5 : 5-diacridyl-dimethochloride* (zinc double salt) which may be regarded as “Bis-Trypaflavin” (P. Ehrlich and L. Benda, Ber. 1913, **46**, 1946).

“Diacridines” possessing structures represented by the formulæ :



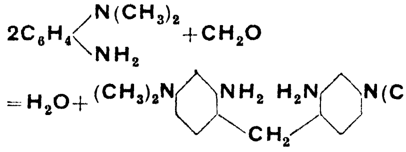


were formed by reducing 2 : 4-dinitrobenzyl chloride in presence of 2 : 7- and 2 : 3-dihydroxynaphthalenes (C. Baezner, Ber. 1906, **39**, 2650).

ACRIDINE DYESTUFFS.

Reference has already been made to the absorption spectra of acridine and various derivatives. The base is colourless but gives bands in the ultra-violet, the salts, and quaternary ammonium compounds are coloured but do not possess tinctorial properties. In order to obtain dyestuffs, the introduction of auxochromic (amino) groups is necessary and the amino-acridines are usually obtained by synthesis. The α-nitroacridine of Graebe and Caro was reduced to an amino-acridine by Anschütz (Ber. 1884, **17**, 437), and Bernthsen found that the trinitro-derivative obtained by nitration of phenyl-acridine could be reduced to a compound which dyed silk yellow (Annalen, 1884, **224**, 30) ; no use seems to have been made of these observations. One dyestuff of the acridine series, *chrysaniline*, is formed in the rosaniline melt (Hofmann, Jahresber. 1862, 346).

Dyestuffs of the acridine series became available when it was found that the condensation products of aldehydes and *m*-diamines lost ammonia with formation of dihydroacridines (*see General Syntheses*, 11). The method has limitations, thus *m*-toluylenediamine and dimethyl-*m*-phenylenediamine condense smoothly with formaldehyde but *m*-phenylenediamine does not (R. Meyer and R. Gross, Ber. 1899, **32**, 2365). The compound formed according to the equation :



can be converted into acridine orange in the same way that tetraminoditolylphenylmethane is converted into benzoflavine. The reaction between aldehyde and *m*-diamine may be carried out in two stages (Meyer and Gross, *l.c.*), thus a monobenzylidene derivative of *m*-toluylenediamine can be converted into tetraminoditolylphenylmethane by warming its alcoholic solution with the hydrochloride of the base to 60°–70°. All the above-mentioned syntheses lead to symmetrically substituted acridines. When less symmetrical dyes are required other methods are often employed, this is also the case where the substituent in position 5 is an aminoaryl group. A number of acridines substituted in 3 and 8 (also 5) have been made from the corresponding acridones.

Acridine dyes have been examined with regard to their photosensitising properties but have not found much application ; they are effective in the green and greenish-yellow. (*See* R. Schuloff, Ausführliches Handbuch der Photographie, Eder and Lüppo-Cramer, III, 3, pp. 92–103 ; Halle, 1932. For their action as desensitisers, *see* F. M. Hamer, Proc. 7th Internat. Congress of Photography, 1928, **92**, and R. Schuloff, *l.c.* 168.) The use of acridine derivatives as antiseptics is referred to below.

In the following descriptions of dyestuffs the order followed depends roughly on whether the hydrogen atom in position 5 is (i) unsubstituted, (ii) replaced by an aryl group, (iii) replaced by an aminoaryl group.

Acridine Yellow (G, R, T. Farbwerk Mühlheim vorm. A. Leonhardt), $C_{15}H_{16}N_3Cl$, is 2 : 8-diamino-3 : 7-dimethylacridine hydrochloride and was discovered by Bender in 1889 (G.P. 52324 ; *cf.* G.P. 149409 of Geigy, Lymn, J.S.C.I. 1897, **16**, 406 ; Ullmann and Marić, Ber. 1901, **34**, 4308 ; Haase, Ber. 1903, **36**, 589). *Preparation :* Tetraminoditolylmethane is prepared by dissolving 125 parts of *m*-toluylenediamine in 50 parts of sulphuric acid and 400 parts of water at 60° and adding 37·5 parts of formaldehyde (40%) in 100 parts of water. The separated sulphate is washed and ground up with ammonia ; 6 parts of the product are dissolved in 20 parts of 20% hydrochloric acid and heated for 3 to 4 hours at 150°. After cooling, the dihydroacridine is separated and dissolved in 200 parts of hot water and ferric chloride added until there is no further increase in the reddish-yellow precipitate (Möhlau-Bucherer, Farbenchemisches Praktikum, 3, Aufl. 1926, 281).

The dye is a yellow powder, the aqueous solution is yellow with green fluorescence. Cotton mordanted with tannin and antimony is dyed yellow, silk greenish-yellow with green fluorescence. The free base forms yellow crystals, soluble in acetone, alcohol, and pyridine.

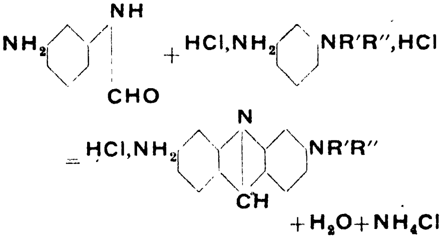
Acridine yellow can be converted into other dyes by a variety of processes. The following may be mentioned : (1) heating with mineral acids under pressure it yields aminohydroxy- and dihydroxy-dimethylacridine (G.P. 121686) ; (2) heating with chloroacetic acid and water under pressure (G.P. 133788, 136729) ; (3) heating with formaldehyde and mineral acids under pressure (G.P. 135771) ; (4) treating with formaldehyde and aromatic bases (G.P. 131365, 132116) ; (5) heating with benzyl chloride in presence of nitrobenzene (J.S.C.I. 1902, **21**, 701, 1536) ; (6) heating with glycerol at 150°–180° (G.P. 151206, constitution of resultant dye unknown) ; (7) alkylation (Ullmann and Marić, *l.c.*, G.P. 79703) ; (8) indirect alkylation by an aldehyde and subsequent reduction (Kyrides and Nat. Aniline and Chem. Co. Inc., U.S.P. 1822490).

Auracin G.—Discovered by Nastvogel in 1902 ; Bayer & Co., G.P. 140848. The formate of acridine yellow, it dyes cotton on a tannin-antimony mordant. Similar products are obtained from the other monobasic fatty acids and acridine yellow base ; as well as from benzoflavine (G.P. 142453).

Acridine Orange, $C_{17}H_{20}N_3Cl,ZnCl_2$, is tetramethyldiaminoacridine zinc chloride and was discovered by Bender in 1889 (Brit. P. 8243, 1890 ; G.P. 59179, 67126). Marks 2G, N, NO (Farbw. Mühlheim) refer to the product obtained by condensation of formaldehyde with *as*-dimethyl-*m*-phenylenediamine followed by elimination of ammonia and oxidation of the resulting dihydroacridine. Alternatively, formaldehyde is condensed with dimethylaniline, the product dinitrated and then reduced to tetramethyl-tetraminodiphenylmethane. Subsequent treatment is the same. Other marks are known as *Euchrysin* 3R (Badische), *Rhodulin Orange* N, NO (Bayer & Co.), *Pharma Acridine Orange* R, RRR (Pharma Chem. Corp., N.Y.). *New Acridine Orange* R (Farbw. Mühlheim) is of similar type. The orange-yellow powder dissolves in water with orange-yellow colour and green fluorescence ; caustic soda gives a yellow precipitate, the solution in concentrated sulphuric acid is nearly colourless but fluoresces green. Cotton is dyed on a tannin-antimony mordant; it is used in cotton printing and colouring of leather and paper.

If the nitration of tetramethyldiaminodiphenylmethane is carried out with an excess of nitric acid, the acridine dye eventually obtained gives red-brown or copper-brown shades on mordanted cotton. It appears that the methyl groups are attacked. Similar results are obtained by nitrating acridine orange, reducing to a leuco-compound and oxidising with ferric chloride (Durand and Huguenin, B.P. 316315, 1929 ; 357060, 1931).

Asymmetrically alkylated derivatives of acridine yellow were patented by A.-G. für Anilin-Fabr. (G.P. 292848, 1915) ; they are stated to be useful for leather goods on account of their evenness in dyeing and insensibility to lime. They are obtained by condensation of formyl derivatives of a *m*-diamine with mono- or di-alkylated *m*-diamines.



Acridine Scarlet, R, 2R, 3R, are mixtures of Acridine Orange NO with pyronine.

Coriphosphin O (and BG), $C_{16}H_{18}N_3Cl$, was discovered by Nastvogel in 1900 (Bayer & Co., G.P. 133709, 161699 ; B.P. 11035, 1900). It is probably 2-amino-3-methyl-8-dimethylamino-acridine hydrochloride since it is obtained by the condensation of *m*-toluylenediamine, *as*-dimethyl-*m*-phenylenediamine, and formaldehyde, followed by ring closure with elimination of ammonia and hydrogen. The solution is orange-red with yellowish-green fluorescence and dyes tannined cotton bright yellowish-brown and leather an even yellow.

Benzoflavine (several marks), 2 : 8-diamino-3 : 7-dimethyl-5-phenylacridine hydrochloride, was discovered by Rudolph in 1887 and introduced commercially by K. Oehler in 1888 (G.P. 43714, 43720, 45294, 45298). For preparation, *see General Syntheses* (11). The dye, which is usually mixed with dextrin, forms an orange powder, difficultly soluble in cold water, more easily in hot. Both aqueous and alcoholic solutions are orange with strong green fluorescence. Hydrochloric acid gives an orange precipitate, sodium hydroxide liberates the yellowish-white base. The solution in concentrated sulphuric acid is greenish-yellow and shows a very strong green fluorescence. It may be used for dyeing mordanted and unmordanted cotton. The acetate and lactate are more easily soluble (G.P. 142453) ; it behaves like acridine yellow when heated with glycerol. Other reactions are described by Hewitt and Fox (J.C.S. 1905, **87**, 1058) and Dunstan and Cleaverley (J.C.S. 1907, **91**, 1619).

Acridine Orange R (Farbwerk Mühlheim and others), $C_{25}H_{24}N_3Cl$, was discovered by Bender in 1889 (B.P. 8243, 1890 ; G.P. 68908, 70065, 71362). This dye is the 5-phenyl derivative of tetramethyldiaminoacridine and is prepared from *as*-dimethyl-*m*-phenylenediamine and benzaldehyde. It is an orange-yellow powder, its solutions in water and alcohol are orange-yellow with green fluorescence, and it dyes cotton on a tannin-antimony mordant.

In G.P. 68908 *m*-aminodimethyl-*o*-toluidine is condensed with *p*-nitrobenzaldehyde to a triphenylmethane derivative, the nitro-group reduced and condensation and oxidation effected in the usual way, yielding an acridine dyestuff possessing two tertiary and one primary amino-groups (G.P. 70065 ; *cf.* G.P. 71362). The use of acetaldehyde as a component was claimed by the Ges. f. Chem. Ind. Basel (G.P. 143893).

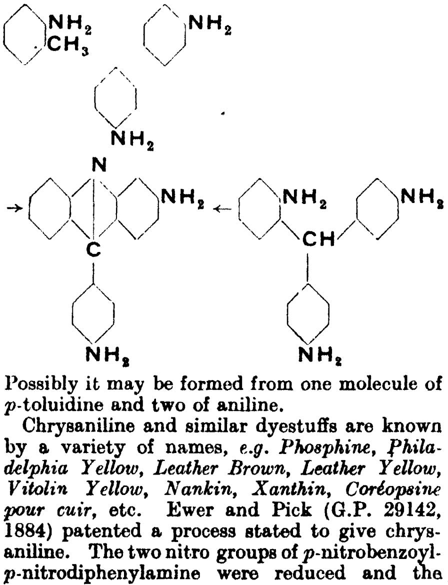
Brilliant Phosphines and Patent Phosphines.—A number of dyestuffs have been prepared by the alkylation of acridine yellow and benzoflavine. It is stated that alkylation of the amino-groups occurs on treatment with alcohols and mineral acids or with alkyl halides, whilst true acridinium salts are formed when methyl sulphate or toluene-*p*-sulphonate are employed (Ges. f. Chem. Ind. Basel, G.P. 79703 ; Farbw. Mühlheim, G.P. 131289 ; Cassella, G.P. 135771 ; Bayer & Co., G.P. 142453). Belonging to the same group are *Aurophosphin* G, 4G (A.-G. f. Anilin-Fabr.) ; *Sabaphosphines* G, GG (Sandoz) ; *Patent Phosphines* A, G, GG, N, R (Ges. f. Chem. Ind.) and sundry Phosphines and *Pharma Phosphines* of the Pharma Corporation. Brilliant Phosphine, 5G of Farbw. Mühlheim and Ges. f. Chem. Ind. is probably prepared according to G.P. 131289 (addition to 79703). The claim is for the further alkylation of aminoacridinium salts. *Brilliant Phosphine* 5G is a bright brown powder, the yellow aqueous solution shows green fluorescence on dilution. It dyes tannined cotton a lively orange-brown and is chiefly used for colouring leather.

Bayer & Co. (G.P. 141297) condense *p*-benzylamino-*o*-toluidine with formaldehyde, the resulting dibenzyltetraminoditolylmethane gives an acridine with two benzyl groups which is disulphonated. The dye gives clear yellow shades on wool, silk and leather and is distinguished by its solubility.

Acridine Scarlet J (Durand and Huguenin) was discovered by C. Vaucher and R. Speitel in 1920 (G.P. 360664 ; B.P. 165721 ; *cf.* B.P. 194165 of Green, Adams, and B. D. C. Corp). It appears to be the hydrochloride of dibromotetramethyldiaminodiphenylacridine and is obtained by brominating solutions of Acridine Orange R in sulphuric acid or nitrobenzene.

It forms a red powder giving orange-red aqueous and alcoholic solutions. The yellow solution in concentrated sulphuric acid shows green fluorescence. It colours tannined cotton, silk, and leather scarlet, is used in cotton printing and is fast to chlorine.

Chrysaniline, $C_{19}H_{15}N_3,HNO_3$, is the nitrate of 5-*p*-aminophenyl-2-aminoacridine and is produced in small amount in the rosaniline melt. Hofmann prepared numerous salts and assigned the formula, $C_{20}H_{17}N_3$, to the base (Z. f. Chem. 1863, **6**, 33). The nitrate, as obtained from the rosaniline residues, crystallises well but is not homogeneous; the pure base has the formula $C_{19}H_{15}N_3$ (O. Fischer and G. Körner, Ber. 1884, **17**, 204). When heated with hydrochloric acid at 180°, one amino-group is replaced by hydroxyl; both of the amino-groups can be eliminated by diazotisation and boiling with alcohol yielding 5-phenylacridine. Since chrysaniline was also produced on fusing *o*-*p*-*p*′-triaminotriphenylmethane with arsenic acid, the constitution was proved and the formation in the rosaniline melt explained.

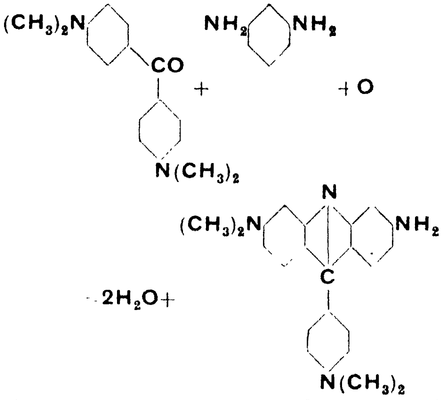


Possibly it may be formed from one molecule of *p*-toluidine and two of aniline.

Chrysaniline and similar dyestuffs are known by a variety of names, *e.g.* *Phosphine*, *Philadelphia Yellow*, *Leather Brown*, *Leather Yellow*, *Vitolin Yellow*, *Nankin*, *Xanthin*, *Coréopsine pour cuir*, etc. Ewer and Pick (G.P. 29142, 1884) patented a process stated to give chrysaniline. The two nitro groups of *p*-nitrobenzoyl-*p*-nitrodiphenylamine were reduced and the resultant *p*-aminobenzoyl-*p*-aminodiphenylamine condensed by heating with zinc chloride at 250°–270°. The compound could not have had the two amino-groups in the positions they occupy in chrysaniline but condensation of *p*-aminobenzaldehyde with *m*-aminodiphenylamine should give the desired result (Badische Co., G.P. 94951, 102072).

Flavophosphine, $C_{20}H_{17}N_3$, m.p. 230°, is probably 7-methylchrysaniline as it is obtained by melting together *m*-nitraniline and *p*-toluidine in presence of hydrochloric acid and ferric chloride (Farbw. vorm Meister, Lucius, and Brüning, G.P. 65985, 1892). The nitraniline may be replaced by *m*-nitrophenol (G.P. 78377, 1894).

Rheonine, 2-Amino-8-dimethylamino-5-*p*-dimethylaminophenylacridine, is formed from *m*-aminophenylauramine or from tetramethyldiaminobenzophenone and *m*-phenylenediamine by condensing with zinc chloride at 200°.



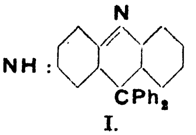
The first 2 : 8 : 5-*p*-triamino derivatives of phenylacridine were discovered by C. Rudolph (Oehler, G.P. 45294), *p*-nitrobenzaldehyde being condensed with *m*-toluylenediamine followed by reduction, condensation, and oxidation.

Flaveosin.—By condensation of *m*-acetaminodimethylaniline with phthalic anhydride (G.P. 49850) the acetyl groups are eliminated and 2 : 8-dimethyldiamino-5 - *o* - carboxyphenylacridine produced. For properties, *see* Grandmougin and Lang, Ber. 1909, **42**, 4014; *cf.* G.P. 73334, 75933, 141356.

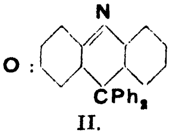
Corioflavines.—Marks G, GG, R, RR (Griesheim-Elektron). These dyestuffs are used in leather dyeing and calico printing. They form red or reddish-brown powders which dissolve in concentrated sulphuric acid with yellow or orange colour and green fluorescence; these solutions turn red or reddish-brown on dilution.

The acridine nucleus is found fused with other (*e.g.* anthraquinone) nuclei in several vat-dyes (*q.v.*).

Carbazines and Carbazones.—These compounds contain the same skeleton of carbon and nitrogen atoms as acridine; though coloured they have no tinctorial properties but are of interest as affording cases of colour in compound in which orthoquinonoid structure is excluded (F. Kehrmann and co-workers, Helv. Chim. Acta, 1919, **2**, 379; 1921, **4**, 26, 538; 1925, **8**, 23, 27; 1926, **9**, 216, 221, 222, 227). Carbazine (I) and carbazone (II) are comparable with aposafranine and aposafranone.



I.



II.

ACRIDINE DRUGS.

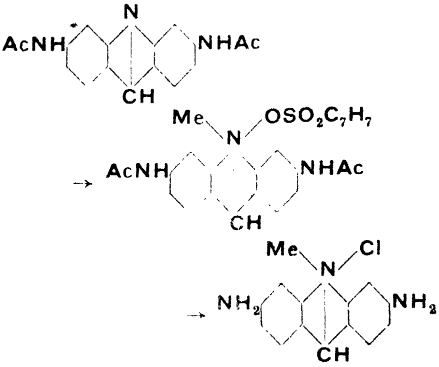
Attention was called to the trypanocidal action of 2 : 8-diamino-10-methylacridinium salts by L. Benda (Ber. 1912, **45**, 1787). These salts find increasing use as antiseptics for they act more effectively in blood serum than in water; they have moreover a low toxicity (Browning, Gulbransen, Kennaway, and Thornton, Brit. Med. J. 1917, i, 73). Whilst amino-groups increase antiseptic action, the effect is weakened by alkylation, acetylation, or replacement by hydroxyl (Browning, Cohen, Gaunt, and Gulbransen, Proc. Roy. Soc. 1922 [B], **93**, 329). A pharmacological comparison has been made of 2 : 8 dimethylacridinium chloride (*proflavine*), 2 : 8-diamino-10-methylacridinium chloride (*trypaflavin* or *acriflavine*); *acridine yellow*, 2 : 8 diamino-3 : 7 : 10-trimethylacridinium nitrate; *brilliant phosphine nitrate*, *argoflavin* (the silver double salt of trypaflavin) and *septacrol* (addition product of silver nitrate and brilliant phosphine nitrate) (E. Lenz, Z. ges. exp. Med. 1921, **12**, 195). In the case of infusoria, acriflavine and proflavine increase the lag period before multiplication begins normally and also affect the subsequent rate of multiplication (T. B. Robertson, Austral. J. Exp. Biol. Med. Sci. 1925, **2**, 21).

Two more recent drugs are *rivanol* (3-ethoxy-5 : 8-diaminoacridine and *atebrine* (3 methoxy-5-δ-diethylamino-α-methylbutylamino-8-chloro acridine), the former is active against *streptococci* whilst atebrine resembles quinine as an anti-malarial acting on the asexual form (schizonts) of the parasite (J. Aeschlimann, J.S.C.I. 1935, T, 135 ; F. L. Pyman, Chem. and Ind. 1935, 584). Several references are given in Aeschlimann's paper.

Proflavine, 2 : 8-diaminoacridine. Since *m*-phenylenediamine condenses with aldehydes to give a mixture of products, *pp'*-diaminodiphenyl methane is nitrated in cold sulphuric acid to give *oo'*-dinitro-*pp'*-diaminodiphenylmethane. On reducing with tin and hydrochloric acid and heating the resulting solution for four hours at 135°, the stannichloride of diaminoacridine is obtained (Cassella & Co., G.P. 230412). The use of *m*-phenylenediamine for the production of 2 : 8-diaminoacridine is claimed by Poulenc Frères and Robert Meyer (B.P. 137214). *m*-Phenylenediamine is melted with formic or oxalic acid at 130°, calcium chloride or zinc chloride being added as a condensing agent. When the evolution of carbon dioxide has ceased, the temperature is raised to 150°–170° (or 190°) and maintained during two hours. The product is purified by means of the sparingly soluble sulphate; yields up to 60% of the theoretical are claimed.

Acriflavine, Trypaflavine, or Flavine, 2 : 8-diamino-10-methylacridinium chloride. Proflavine is diacetylated and then methylated on the 10-nitrogen atom with methyl *p* toluene-sulphonate. The acetyl groups are then removed by heating with a mixture of equal volumes of water and hydrochloric acid (*d* 1·18) (*v. infra*).

Amino-groups are also protected against alkylation if ortho-methyl groups are present. H. Grünhagen (A.-G. für Aniline-Fabr., G.P. 366096) finds that methyl chloride and ethyl bromide act only on the cyclic nitrogen atom of 3 : 7-dimethyl-2-dimethylamino-8-aminoacridine. The product is a yellow dye for leather, it might find application as an antiseptic. I.G. Farbenind. A.-G. (G.P. 344627) claim that 2 : 8-diaminoacridine is alkylated at 90°–100° with an alkyl sulphate or arylsulphonate in absence of a solvent (if desired, in presence of an inorganic salt) the ring nitrogen atom and one amino-group are alkylated. The dyeing properties are given.



Alkylation of proflavine to **acriflavine** is usually incomplete. The analysis of "**flavines**" is dealt with by E. L. Howes (Ind. Eng. Chem. (Anal.), 1930, **2**, 114) ; P. J. Udall (Analyst, 1932, **57**, 295) ; A. D. Powell and G. F. Hall (Quart. J. Pharm. 1933, **6**, 389 ; 1934, **7**, 522) ; M. Gailliot (*ibid.* 63 ; Bull. Soc. chim. 1934 [v], **1**, 796) ; J. Marshall (Quart. J. Pharm. 1934, **7**, 514) ; F. Reimers (Quart. J. Pharm. 1935, **8**, 218).

Much attention has been paid to the preparation of solutions of acridine compounds from the points of view of sufficient solubility, stability, and bactericidal efficiency. Chem. Fabr. vorm. Sandoz (B.P. 283184) claim that powerfully anti-parasitic compounds are obtained by combination of amino and diamino-acridines, their alkyl halides and alkyloxy derivatives with bile acids (desoxycholic acid excluded). I.G. Farbenind. A. G. (B.P. 405629, *cf.* 419603, 419632, 421175) prepare salts of organic arsonic acids. The same firm (B.P. 328212, 345631, 348047) describe double salts containing both 2 : 8-diamino-10-alkylacridinium salt and 2 : 8-diaminoacridine salt. These are claimed as valuable bactericidal agents, more soluble than the components. The existence of a molecular compound of the hydrochloride and the methochloride has been denied by Gailliot (Quart. J. Pharm. 1934, **7**, 63) though it is admitted that the mixtures are more soluble (Bull. Soc. chim. 1934 [v], **1**, 796). I.G. Farbenind. A.-G. (B.P. 342690, 395405) claim the stabilisation of solutions of salts of the above compounds by the addition of small amounts of a reducing agent, *e.g.* sodium bisulphite or hydrosulphite. The ***methanesulphonate*** ($+0{\cdot}5H_2O$) of 3 : 6-diamino-10-methyl acridinium gives a thermally stable, neutral solution in twice its weight of water at 20° (May and Baker, and R. W. E. Stickings, B.P. 439902). L. Cassella (G.P. 375790) describes acridinium palmitates and stearates which are oil- and fat-soluble and suitable for use in dermatology. Solutions of salts with fatty acids or sulpho-fatty acids are dissolved in solutions of sodium salts of the same or different acids (I.G. Farbenind. A.-G., B.P. 412176, *cf.* B.P. 382889). Cassella (G.P. 392066, 408868) recommends dihydroxy- (and dialkyloxy-) acridine and acridinium salts as antiseptics.

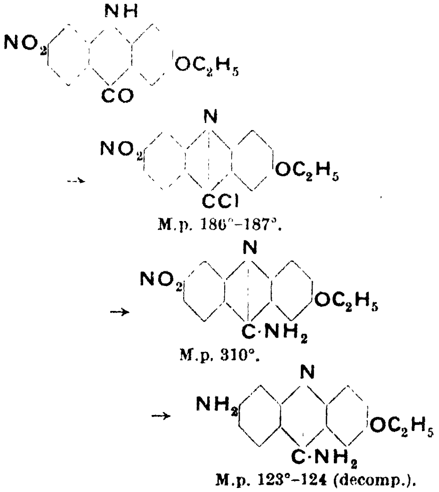
The isomerides of proflavine and acriflavine with amino groups in position 3 and 7 have been obtained by M. T. Bogert, A. D. Hirschfelder, and P. G. I. Lauffer (Coll. Czech. Chem. Comm. 1930, **2**, 383). 3 : 7 Dinitroacridone is formed by cyclisation of 2-*p*-nitroanilino-5-nitrobenzoic acid and reduced successively to 3 : 7-diaminoacridone, m.p. 325° and diaminoacridine, m.p. 318°. The methochloride is obtained through the diacetyl-derivative. The bactericidal properties of these compounds are inferior to those of the corresponding 2 : 8-isomerides.

2 : 6-*Diaminoacridine*, m.p. 213°–216° (decomp.) has been prepared by A. Albert and W. H. Linnell with a view to examining its bactericidal properties. 3 : 3′-Dinitrodiphenylamine-2 carboxylic acid was cyclised (phosphoryl chloride) to 5-chloro-2 : 6-dinitroacridone (m.p. 200°-203°), which was hydrolysed to dinitroacridone. Successive reductions gave 2 : 6-diaminoacridone, m.p. 306°, and 2 : 6-diaminoacridine (J.C.S. 1936, 88).

Other derivatives of 2 : 8-diamino-10-methyl acridinium chloride are mentioned by Cassella (G.P. 354400) and Brit. Dyestuffs, Ltd., W. H. Perkin, and A. W. Burger (B.P. 248182). The last named have prepared 3 : 7-diethoxy-2 : 8 diamino-10-methylacridinium chloride which is stated to be specially suitable and to have the requisite solubility for medical purposes.

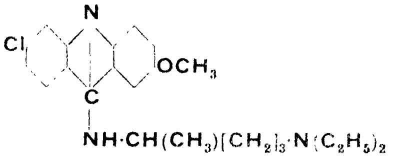
Further patents dealing with acridine bactericides are B.P. 347515, B.P. 283184, B.P. 367024, 419603, U.S.P. 1738449.

Rivanol, 3 ethoxy-5 : 8 diaminoacridine is prepared by the following series of reactions (Farbw. vorm. Meister, Lucius, and Brüning, B.P. 176038). 2-Chloro-4-nitrobenzoic acid is condensed with *p*-phenetidine and the resulting 2-*p*-phenetidino-4 nitrobenzoic acid cyclised. The remaining reactions follow the course :



Both acetates and lactates, especially the former, of 5-amino-acridines are readily soluble (I.G. Farbenind. A.-G., B.P. 337136).

Atebrine has the constitution



and is the most important of the numerous acridine (and quinoline) derivatives with basic side chains synthesised by Schulemann, Schönhofer, and Winkler (I.G.) and tested by Roehl and Kikuth on canaries infected with *Plasmodium præcox*. It is prepared from the 3 methoxy-5 . 8-dichloroacridine, m.p. 160° 161°, obtained by the usual methods from 2 : 4-dichlorobenzoic acid and *p*-anisidine (I.G. Farbenind. A.-G., B.P. 353537, 363392, *cf.* 304280). This is then condensed with δ diethylamino α methylbutylamine which is obtained by reduction of methyl γ-diethylaminopropyl ketone in presence of ammonia. The production of the ketone follows the scheme :

$$Et_2N{\cdot}C_2H_4Cl + CHNaAc{\cdot}CO_2Et$$
$$\xrightarrow{-NaCl} Et_2N{\cdot}C_2H_4{\cdot}CHAc{\cdot}CO_2Et$$
$$\xrightarrow{+H_2O\ -CO_2\ -EtOH} Et_2N{\cdot}C_2H_4{\cdot}CH_2{\cdot}CO{\cdot}Me$$

(Miess and Mauss, Z. angew. Chem. 1934, **47**, 636 ; Ber. 1936, **69** [B], 534 ; J. Aeschlimann, *l.c.* ; *see also* Magidson and co-workers, Arch. Pharm. 1933, **271**, 359 ; 1934, 272, 74 ; Ber. 1936, **69** [B], 396, 537 ; Khim. Pharm. Prom. 1933, 187 ; L. Monti, Gazzetta, 1933, **63**, 724 ; Jensen and Howland, J. Amer. Chem. Soc. 1926, **48**, 1988 ; B. Samdahl and C. F. Weider, Bull. Soc. chim. 1935 [v], **2**, 2008 ; J. C. Feldman and E. L. Kopeliovitsch, Arch. Pharm. 1935, **273**, 488.)

1-(*β-Diethylaminoethyl*) *aminoacridine*, b.p. 180/1mm., is obtained from 1-aminoacridine, chloroethyldiethylamine hydrochloride and sodium acetate (G. R. Clems and W. Hook, J.C.S. 1936, 608).

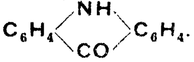
The hydrochlorides of 1-, 2-, and 3-acridylarsinic acids have been prepared by S. M. Scherlin and co-workers (Annalen, 1935, **516**, 218).

J. T. H.

ACRIDINE SCARLET *v.* ACRIDINE DYESTUFFS.

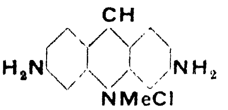
ACRIDONE COLOURS *v.* ANTHRAQUINONE DYESTUFFS.

ACRIDONES. Substances containing the acridone grouping. The parent substance acridone, m.p. 354° is



$C_6H_4\left\langle{NH \atop CO}\right\rangle C_6H_4$.

ACRIFLAVINE, *trypaflavine*, is 2 : 8-diamino-10-methylacridinium chloride,



Antiseptic (*v.* ACRIDINE, *acridine drugs*).

ACRINYL THIOCYANATE,

$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CNS$,

and acrinyl *iso*thiocyanate $C_7H_7O{\cdot}NCS$ are constituents of white mustard oil.

ACROLEIN, *propenal, acraldehyde,*

$CH_2:CH{\cdot}CHO$

is prepared by removing the elements of water from glycerol by distillation in the presence of a dehydrating agent; using anhydrous magnesium sulphate for this purpose Wohl and Mylo (Ber. 1912, **45**, 2406) obtained a 60% yield (*cf. also* Witzemann, J. Amer. Chem. Soc. 1914, **36**, 1766). Moureu and Lepape (Compt. rend. 1919, **169**, 885) employing a mixture of $KHSO_4$ (5 parts) and K_2SO_4 (1 part) with one quarter its weight of glycerol, controlling the heating and replacing the glycerol as required secured a 67·5% yield. Schering-Kahlbaum A.-G. (B.P. 346221) describe a manufacturing process in which glycerol vapour is led over a salt of a tribasic (or higher) acid (Li, Cu, Bi, Ag, or Fe phosphate, Mg borate, etc.) preferably on a carrier (pumice) at 400°–500°. Salway (J.C.S. 1916, **109**, 138) found that acrolein is one of the products of oxidation of linolenic acid and of oils containing the glycerides of this acid.

Acrolein is a liquid with an irritating odour. It was used extensively under the name "aquilit" as a lachrymator by the French during the war. It has m.p. $-88°$ to $-87°$; b.p. 52·15°/751·3 mm., 52·46°/760 mm., 53·00°/773·2 mm.; *v.p.* in kg./sq. cm. 0·148/5°, 0·235/15°, 0·366/25°, 0·923/50°, 4·18/100°, 6·91/120°, 10·0/137·2°; d^0 0·86205, d^{15} 0·8447, d^{30} 0·8269, d^{50} 0·8075; n_D 1·4066/11·5°, 1·40475/15°, 1·4041/16·2°, 1·4022/19·3°. The latent heat of vaporisation at the b.p. is 120·7 cal. per g. (Moureu, Boutaric, and Dufraisse, J. Chim. phys. 1920, **18**, 333). Over a range of $-8°$ to $+53°$ water becomes more soluble in acrolein with rise of temperature, whilst acrolein becomes less soluble, the amount of water in 100 g. of each phase is at 0° 4·67 and 79·36 g., and at 50° 12·38 and 77·04 g. respectively (Boutaric, *ibid.* 126). Acrolein when kept undergoes spontaneous change in one of two directions, giving either an insoluble resin, *disacryl*, or a soluble resin. The presence of impurities, rise in temperature or increase in intensity of illumination accelerate the former change, whilst the latter is induced by the presence of a free base, certain metallic salts or hydrogen sulphide. The crude aldehyde can be stabilised by shaking with 10% of its weight of dry sodium hydrogen carbonate; the product so obtained is stable for a long time in absence of air and sunlight, and at a temperature not exceeding 30° (Moureu, Dufraisse, and Lepape, Compt. rend. 1919, **169**, 621, 705). Acrolein can also be stabilised by the addition of a small quantity (1 : 4,000) of a polyphenol (Moureu and others, Compt. rend. 1920, **170**, 26).

Antiseptic action.—Berthelot (Rev. hyg. 1922, **44**, 16) has shown that acrolein (stabilised by the addition of 0·2% of catechol), both in aqueous solution and as a vapour, is inferior to formaldehyde in its germicidal and inhibitory powers.

Chemical properties.—Acrolein is readily oxidised even in the air to *acrylic acid,*

$CH_2:CH{\cdot}COOH$;

and catalytic hydrogenation in the presence of nickel at 50°–60° reduces it to propaldehyde, $CH_3{\cdot}CH_2{\cdot}CHO$.

Acrolein readily absorbs bromine to form $\beta\gamma$-dibromo-propaldehyde,

$CH_2Br{\cdot}CHBr{\cdot}CHO$,

b.p. 86·4°, d^{15} 2·198, which readily loses HBr on distillation with an aqueous solution of sodium acetate to form *α-bromo-acraldehyde,*

$CH_2:CBr{\cdot}CHO$,

a colourless mobile liquid, b.p. 28·5°/11 mm., 111°/420 mm., *d* 1·68, having an intensely irritating odour and lachrymatory action; it absorbs bromine to form *ββγ-tribromopropaldehyde*, b.p. 85·5°/11 mm. and *d* 2·51 (Piloty and Stock, Ber. 1898, **31**, 1385).

Detection and estimation.—The aldehyde vapour is condensed in distilled water through which a slow stream of oxygen is passed until the solution is strongly acid. On dissolving freshly precipitated silver oxide in the liquid and concentrating the clear solution, pure silver acrylate crystallises out (Œchsner de Coninck, Bull. Acad. roy. Belg. 1912, 524; A. 1913, ii, 79). A delicate test for acrolein is afforded by the colour produced when the liquid to be tested is heated with 1–2 c.c. of an aqueous solution of resorcinol and a few drops of 10% solution of sodium hydroxide; after two minutes a bluish green colour appears in a dilute and a red colour in a concentrated solution; the colour is destroyed by acids but restored by alkalis (Tsalapatanis, Anal. Asoc. Quím. Argentina, 1917, **5**, 244; A. 1920, ii, 394). A colorimetric method for estimating acrolein by means of Schiff's reagent, which is independent of the presence of stabilisers of the polyphenol type, is described by Moureu and Boismenu (J. Pharm. Chim. 1923 [vii], **27**, 49, 89).

Acrolein Resins.—The polymerisation of acrolein gives a white powder soluble in most organic solvents to yield a lacquer. Acrolein also condenses with phenol giving a moulding resin of use as electrical insulating material, marketed under the name of *Orcas*. *Acrolite* is another moulding resin prepared from glycerol, phenol, and sulphuric acid (McIntosh, Ind. Eng. Chem. 1927, **19**, 111). M. A. W.

ACROLITE *v.* ACROLEIN.

α- and **β-ACROSE**, $C_6H_{12}O_6$. By condensation of either acrolein dibromide, formaldehyde, glycerose or glycollic aldehyde with alkali, generally baryta water, a mixture of inactive hexose sugars is obtained. This is Emil Fischer's original synthesis of the sugars. The one product termed α-acrose is *dl*-fructose, the other β-acrose is *dl*-sorbose (Küster and Schoder, Z. physiol. Chem. 1924, **141**, 110).

The sugar produced by polymerisation of formaldehyde by ultra-violet light (Baly, J.C.S. 1921, **119**, 1025) is not α- or β-acrose.

The chemical polymerisation is regarded as a condensation of glyceraldehyde with dihydroxyacetone; evidently under the influence of ultra-violet light the condensation does not proceed in the same way (*see* E. F. and K. F. Armstrong, "The Carbohydrates," pp. 72–75, Longmans, 1934). E. F. A.

ACRYLIC ACID, *propene acid, vinylformic acid*, $CH_2 : CH{\cdot}COOH$, is formed by oxidising acrolein with silver oxide and is most conveniently prepared from glycol-chlorohydrin through the cyanide :

$$HO{\cdot}CH_2{\cdot}CH_2Cl \rightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \rightarrow CH_2 : CH{\cdot}COOH$$

(van der Burg, Rec. trav. chim. 1922, **41**, 21). The acid has m.p. 13°, b.p. 141°, d_4^{16} 1·0621, n_D^{20} 1·4224, $K = 5{\cdot}6 \times 10^{-5}$ at 25° ; it polymerises slowly on standing, and rapidly at the boiling-point. It yields propionic acid on reduction, and the β-halogenopropionic acid with the corresponding halogen acid.

The alkyl esters of substituted acrylic acids are mobile liquids and certain of them, notably ethyl and methyl acrylate,

$$CH_2 : C(Me){\cdot}COOEt,$$

which boils at 117°–120°, set to a glass-like resin on standing (Howles, Thorpe, and Udall, J.C.S. 1900, **77**, 947). These substances have acquired considerable value as thermo-plastics.

ACTAEA RACEMOSA, *Cimicifuga.* (Black Snakeroot, Black Cohosh.) The drug is the dried root of *Cimicifuga racemosa.* It contains much resin, *iso*ferulic acid, a trace of salicylic acid, a phystosterol, palmitic acid and three crystalline bodies, apparently alcohols. Used as a bitter and expectorant.

ACTEROL. Trade name for irradiated ergosterol, *i.e.* ergosterol which has been exposed to ultra-violet light for the production of vitamin D.

ACTINIOERYTHRIN. The carotenoid pigment of the sea anemone, *Actinia equina*, was first described by Fabre and Lederer (Bull. Soc. chim. biol. 1934, **16**, 105) and more fully investigated by Heilbron, Jackson, and Jones (Biochem. J. 1935, **29**, 1384). The pigment, which is an epiphasic ester,[1] forms deep red-black needles from ethyl alcohol, m.p. 83°–85°, and exhibits, in carbon disulphide, absorption maxima at 574, 538, and 497 mμ. On carefully controlled hydrolysis it furnishes a new pigment (*see* VIOLERYTHRIN).

I. M. H. and R. F. P.

ACTINIUM. Symbol **Ac.** Atomic Number 89. Atomic Weight 227±1. A radioactive element discovered by Debierne while working up uranium residues from pitchblende (Compt. rend. 1899, **129**, 593 ; 1900, **130**, 906 ; 1903, **136**, 446 and 767) is identical with the substance *Emanium* described by Giesel (Ber. 1902, **35**, 3608 ; 1903, **36**, 342 ; 1904, **37**, 1696, 3963), who succeeded in freeing his preparations from thorium. Its chemical properties are intermediate between those of lanthanum and calcium. In presence of ammonium salts neither ammonia nor ammonium oxalate precipitate actinium completely, but in presence of manganese it can be precipitated from the basic solution as a manganate, a reaction which proved of great value in its separation (Auer von Welsbach, Sitzungsber. Akad. Wiss. Wien, 1910, **119** [iia], 1 ; A. 1911, ii, 7).

Actinium always occurs in radioactive minerals containing uranium, never in those containing only thorium and it is probably derived from uranium in a branch disintegration series. Boltwood found that the ratio uranium-actinium in aged uranium minerals is fairly constant (Amer. J. Sci. 1906, **22** [iv], 537 ; 1908, **25** [iv], 269 ; A. 1907, ii, 62 ; A. 1908, ii, 454); *see also* McCoy and Ross (J. Amer. Chem. Soc. 1907, **29**, 1709 ; A. 1908, ii, 81). Later work by Meyer and Hess (Sitzungsber. Akad. Wiss. Wien, 1919, **128** [iia], 909 ; A. 1919, ii, 658), Kovarik (Science, 1930, **72**, 122 ; A. 1930, 1495), Holmes (A. 1930, 1339), Gleditsch and Focyn (Compt. rend. 1934, **199**, 412 ; A. 1934, 1053), Bruner and Schlundt (J. Physical Chem. 1934, **38**, 1183 ; A. 1935, 322), Francis and Chang (Compt. rend. 1934, **198**, 733 ; A. 1934, 387 confirm this and indicate that actinium derived from uranium, though the exact pos where branching occurs is still a matt controversy. *See* also Francis and Phil. Mag. 1935 [vii], **20**, 623 ; Elsen, Weekblad, 1935, **32**, 343.

Piccard (Arch. Sci. phys. nat. 1917 [iv 161 ; A. 1918, ii, 6) suggests that actiniu not derived either from uranium-I or fr uranium-II, but from a third isotope of uraniu called *actino-uranium* which does not belong to the uranium-radium family but is a primary radio-element at the head of the actinium family. This is further discussed by Adams (J. Amer. Chem. Soc. 1920, **42**, 2205). Wilkins (Physical Rev. 1927 [ii], **29**, 352 ; A. 1928, 1302) considers that the actinium series arises from an isotope of uranium-I, the decay constant of which is several times that of uranium-I. The problem of the genesis of the actinium series is discussed by Russell (Phil. Mag. 1924 [vi], **46**, 642), Elsen (Z. anorg. Chem. 1929, **180**, 304 ; A. 1929, 737 ; Chem. Weekblad, 1931, **28**, 342, 486 ; A. 1931, 890, 1145 ; Chem. Weekblad, 1935, **32**, 343 ; A. 1935, 900), von Grosse (Z. anorg. Chem. 1930, **186**, 38 ; A. 1930, 515), Walke (Phil. Mag. 1934 [vii], **18**, 256 ; A. 1934, 1053). Imori and Yoshimura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 11) have examined the pleochroic haloes in a number of Japanese biotites and, like Joly (Proc. Roy. Soc. 1922, A, **102**, 682), they found certain haloes which could not be ascribed to members of the uranium- or thorium-disintegration series. The presence of actinium rings unmasked by members of the uranium-radium series is regarded as evidence of the independence of the two series. Further, the rings are ascribed to isotopes of uranium which precede protoactinium in the series as originally postulated by Piccard (*l.c.*). Russell (Nature, 1927, **120**, 545 ; A. 1927, 1003), however, while agreeing with the observations of the Japanese chemists, ascribes the formation of the abnormal haloes to weathering of the radioactive minerals.

Actinium has not been prepared in the pure is derived from the transformation of actinium emanation, and the invisible film is known as the *active deposit* of actinium and emits α-, β-, and γ-rays. Radiation from the active deposit of actinium has been examined by Sevengue, Compt. rend. 1936, **202**, 410.

---

[1] An epiphasic ester is an ester which on partition between alcohol and light petroleum exists in the light petroleum (*see* CAROTINOIDS).

Actinium-A has a very short life with a half-period of 2×10^{-3} sec., an average life period of 3×10^{-3} sec. It emits α-rays having a range of 6·5 cm. in air at 15° (Geiger and Nuttall, Phil. Mag. 1912 [vi], **24**, 647).

Actinium-A rapidly changes into *actinium-B*, this emits feeble β-rays (Graf, Compt. rend. 1933, **197**, 238 ; A. 1933, 334 ; Sargent, Proc. Camb. Phil. Soc. 1929, **25**, 514 ; 1933, **29**, 156 ; A. 1930, 8 ; 1933, 204 ; Lecoin, Compt. rend. 1936, **202**, 1057).

Actinium-B passes into *actinium-C* which emits both α- and β-rays. Marsden and Wilson showed the complexity of the α-particles from actinium-C (Nature, 1913, **92**, 29), and Rutherford, Ward, and Wynn-Williams (Proc. Roy. Soc. 1930, A, **129**, 211 ; A, 1930, 1338) have shown that the 5·5 cm. particles from actinium-C are in two well marked groups of ranges, 5·51 and 5·09 cm. in the ratio of 100 : 2 (*see* Madame Marie Curie and Rosenblum, Compt. rend. 1931, **193**, 848 ; A, 1931, 995). The half-life period is 2·15 min., and the average life period 3·12 min.

Marsden and his co-workers have shown that actinium-C decomposes into two radioactive elements : *actinium-D*, an α-ray product, also called Actinium-C″, and actinium-C′ or actinium-C_2, a β-ray product. Actinium-C′ gives off α-rays with a range of about 6·4 cm. in air at 15° and has a half-life period of 7×10^{-3} sec. The nature of the end product of the α-particle decay of actinium-C′ is not known, though it would appear to be an isotope of lead. Only 2% of the parent actinium-C is converted, the remainder passes into actinium-D, which, on account of its atomic weight, appears to be an isotope of lead. Actinium-D gives off β-rays and passes into *actinium-E*, which has the same atomic weight as actinium-D.

Aston (Nature, 1929, **123**, 313) examined the mass-spectrograph of uranium-lead tetramethyl prepared from bröggerite and found the isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb in the abundance of 86·8, 9·3, and 3·9% respectively. ^{207}Pb cannot be due to ordinary lead, and he concluded that it is the end point of the actinium series. Calculated from his result the atomic weight of protoactinium becomes 231. On the basis of this work Rutherford (Nature, 1929, **123**, 313) suggests that an isotope of uranium-I, actinouranium, of mass 235, atomic number 92 is the head of the actinium series passing to protoactinium via uranium-Y. Although there is agreement that the atomic weight of the actinium-Ω must be accepted as 207, other points have received criticism (*cf.* Fenner and Piggot, *ibid.* p. 793 ; A. 1929, 620 ; Holmes, Nature, 1930, **126**, 348 ; A. 1930, 1339 ; Nature, 1930, **126**, 548 ; A. 1930, 1339 ; Wildish, J. Amer. Chem. Soc. 1930, **52**, 163 ; A. 1930, 308 ; Kovarik, Science, 1930, **72**, 122 ; A. 1930, 1495 ; Amer. J. Sci. 1930 [v], **20**, 393 ; A. 1930, 1552 ; Russell, Nature, 1927, **120**, 402 ; A. 1927, 1002).

Protoactinium, **Pa**, atomic weight 231, atomic number 91, is the immediate disintegration product of uranium-Y (Gratias, Thesis, Oxford, 1932 ; and Gratias and Collie, J.C.S. 1932, 987 ; A. 1932, 443). It was separated from uranium minerals by Hahn and Meitner (Physikal. Z. 1918, **19**, 208 ; A. 1918, ii, 345). Von Grosse (Ber. 1928, **61** [B], 233 ; A. 1928, 259) first prepared it in a weighable amount as the pentoxide by working up large quantities of Joachimstal pitchblende residues. Fusion of the material with potassium carbonate and dissolution of the residues in water removed almost all of the oxides of tantalum and niobium, whereas more than 99% of the protoactinium remained with the insoluble basic oxides, this demonstrates the great difference in basicity between the pentoxides of tantalum and protoactinium. Further concentration showed that protoactinium was remaining quantitatively with the oxides of zirconium and hafnium. The isolation of the first from the other two was effected either by dissolving the oxides in warm dilute hydrochloric acid and precipitating the protoactinium by oxalic acid or by adding thorium oxide to t
mixed oxides and precipitating it as oxala
In the second case 70–90% of the protoacti
was found in the thorium oxalate preci
The thorium was subsequently extract
fluoride and the protoactinium finally
cipitated from the fluoride by ammonia
these processes 2 mg. of protoactinium
oxide were obtained and as its activity co
not be increased by a repetition of the process of concentration the purity of the product was thus assumed. Von Grosse (J. Amer. Chem. Soc. 1930, **52**, 1742 ; A. 1930, 883), working with 10–50 mg. of pentoxide free from other metals, has shown that protoactinium is definitely basic in its properties and is not chemically similar to its homologue tantalum, as has been assumed. They are similar in that both oxides dissolve in 40% hydrofluoric acid and are precipitated by ammonia from mineral acid solutions. Protoactinium oxide is insoluble in molten potassium carbonate in which tantalum oxide is completely soluble, but is almost entirely soluble in molten sodium bisulphate, in which tantalum oxide is nearly insoluble. Protoactinium is precipitated from acid solution by excess of phosphoric acid. There is no corresponding precipitation with tantalum. These observations have been confirmed by Gratias and Gratias and Collie (*l.c.*), using unweighably small quantities of protoactinium. They used an amplifier and an ionisation counter to detect the presence of radioactive materials in the chemical operations.

Protoactinium can be precipitated quantitatively by means of titanium by hydrolysis of slightly acid titanium salts (Mlle. Zavizziano, Compt. rend. 1935, **200**, 1843 ; 1936, **202**, 1052 ; Chang, J. Chinese Chem. Soc. 1935, **3**, 381). The co-precipitation of protoactinium with sulphides of copper, antimony, mercury, and bismuth has been studied by Chang and Houang, Bull. Soc. chim. 1936 [v], **3**, 326 ; *see* also Chang and Li, J. Chinese Chem. Soc. 1936, **4**, 93.

Progress was made in the separation and

is derived from the transformation of actinium emanation, and the invisible film is known as the *active deposit* of actinium and emits α-, β-, and γ-rays. Radiation from the active deposit of actinium has been examined by Sevengue, Compt. rend. 1936, **202**, 410.

Actinium-A has a very short life with a half-period of 2×10^{-3} sec., an average life period of 3×10^{-3} sec. It emits α-rays having a range of 6·5 cm. in air at 15° (Geiger and Nuttall, Phil. Mag. 1912 [vi], **24**, 647).

Actinium-A rapidly changes into *actinium-B*, this emits feeble β-rays (Graf, Compt. rend. 1933, **197**, 238 ; A. 1933, 334 ; Sargent, Proc. Camb. Phil. Soc. 1929, **25**, 514 ; 1933, **29**, 156 ; A. 1930, 8 ; 1933, 204 ; Lecoin, Compt. rend. 1936, **202**, 1057).

Actinium-B passes into *actinium-C* which emits both α- and β-rays. Marsden and Wilson showed the complexity of the α-particles from actinium-C (Nature, 1913, **92**, 29), and Rutherford, Ward, and Wynn-Williams (Proc. Roy. Soc. 1930, A, **129**, 211 ; A, 1930, 1338) have shown that the 5·5 cm. particles from actinium-C are in two well marked groups of ranges, 5·51 and 5·09 cm. in the ratio of 100 : 2 (*see* Madame Marie Curie and Rosenblum, Compt. rend. 1931, **193**, 848 ; A, 1931, 995). The half-life period is 2·15 min., and the average life period 3·12 min.

Marsden and his co-workers have shown that actinium-C decomposes into two radioactive elements : *actinium-D*, an α-ray product, also called Actinium-C″, and actinium-C′ or actinium-C_2, a β-ray product. Actinium-C′ gives off α-rays with a range of about 6·4 cm. in air at 15° and has a half-life period of 7×10^{-3} sec. The nature of the end product of the α-particle decay of actinium-C′ is not known, though it would appear to be an isotope of lead. Only 2% of the parent actinium-C is converted, the remainder passes into actinium-D, which, on account of its atomic weight, appears to be an isotope of lead. Actinium-D gives off β-rays and passes into *actinium-E*, which has the same atomic weight as actinium-D.

Aston (Nature, 1929, **123**, 313) examined the mass-spectrograph of uranium-lead tetramethyl prepared from bröggerite and found the isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb in the abundance of 86·8, 9·3, and 3·9% respectively. ^{207}Pb cannot be due to ordinary lead, and he concluded that it is the end point of the actinium series. Calculated from his result the atomic weight of protoactinium becomes 231. On the basis of this work Rutherford (Nature, 1929, **123**, 313) suggests that an isotope of uranium-I, actinouranium, of mass 235, atomic number 92 is the head of the actinium series passing to protoactinium via uranium-Y. Although there is agreement that the atomic weight of the actinium-Ω must be accepted as 207, other points have received criticism (*cf.* Fenner and Piggot, *ibid.* p. 793 ; A. 1929, 620 ; Holmes, Nature, 1930, **126**, 348 ; A. 1930, 1339 ; Nature, 1930, **126**, 548 ; A. 1930, 1339 ; Wildish, J. Amer. Chem. Soc. 1930, **52**, 163 ; A. 1930, 308 ; Kovarik, Science, 1930, **72**, 122 ; A. 1930, 1495 ; Amer. J. Sci. 1930 [v], **20**, 393 ; A. 1930, 1552 ; Russell, Nature, 1927, **120**, 402 ; A. 1927, 1002).

Protoactinium, **Pa**, atomic weight 231, atomic number 91, is the immediate disintegration product of uranium-Y (Gratias, Thesis, Oxford, 1932 ; and Gratias and Collie, J.C.S. 1932, 987 ; A. 1932, 443). It was separated from uranium minerals by Hahn and Meitner (Physikal. Z. 1918, **19**, 208 ; A. 1918, ii, 345). Von Grosse (Ber. 1928, **61** [B], 233 ; A. 1928, 259) first prepared it in a weighable amount as the pentoxide by working up large quantities of Joachimstal pitchblende residues. Fusion of the material with potassium carbonate and dissolution of the residues in water removed almost all of the oxides of tantalum and niobium, whereas more than 99% of the protoactinium remained with the insoluble basic oxides, this demonstrates the great difference in basicity between the pentoxides of tantalum and protoactinium. Further concentration showed that protoactinium was remaining quantitatively with the oxides of zirconium and hafnium. The isolation of the first from the other two was effected either by dissolving the oxides in warm dilute hydrochloric acid and precipitating the protoactinium by oxalic acid or by adding thorium oxide to tl;f mixed oxides and precipitating it as oxalaes In the second case 70–90% of the protoactinesis was found in the thorium oxalate precil with The thorium was subsequently extracte ob- fluoride and the protoactinium finally a on cipitated from the fluoride by ammonia 226 ; these processes 2 mg. of protoactinium R.P. oxide were obtained and as its activity coti, not be increased by a repetition of the process of concentration the purity of the product was thus assumed. Von Grosse (J. Amer. Chem. Soc. 1930, **52**, 1742 ; A. 1930, 883), working with 10–50 mg. of pentoxide free from other metals, has shown that protoactinium is definitely basic in its properties and is not chemically similar to its homologue tantalum, as has been assumed. They are similar in that both oxides dissolve in 40% hydrofluoric acid and are precipitated by ammonia from mineral acid solutions. Protoactinium oxide is insoluble in molten potassium carbonate in which tantalum oxide is completely soluble, but is almost entirely soluble in molten sodium bisulphate, in which tantalum oxide is nearly insoluble. Protoactinium is precipitated from acid solution by excess of phosphoric acid. There is no corresponding precipitation with tantalum. These observations have been confirmed by Gratias and Gratias and Collie (*l.c.*), using unweighably small quantities of protoactinium. They used an amplifier and an ionisation counter to detect the presence of radioactive materials in the chemical operations.

Protoactinium can be precipitated quantitatively by means of titanium by hydrolysis of slightly acid titanium salts (Mlle. Zavizziano, Compt. rend. 1935, **200**, 1843 ; 1936, **202**, 1052 ; Chang, J. Chinese Chem. Soc. 1935, **3**, 381). The co-precipitation of protoactinium with sulphides of copper, antimony, mercury, and bismuth has been studied by Chang and Houang, Bull. Soc. chim. 1936 [v], **3**, 326 ; *see* also Chang and Li, J. Chinese Chem. Soc. 1936, **4**, 93.

Progress was made in the separation and

purification of large quantities of protoactinium by Graue and Käding (Naturwiss. 1934, **22**, 511 ; A. 1934, 854), and finally Grosse (Proc. Roy. Soc. 1935, A, **150**, 363) succeeded in determining the atomic weight by chemical methods. Owing to scarcity of material available the compound K_2PaF_7 was employed, its stability having been found to be suitable for the purpose. The results agree with the whole number 231 to within the limits of experimental error, and this supports the view that the final product of radioactive disintegration of the series is an isotope of lead of mass 207. Schüler and Gollnow (Naturwiss. 1934, **22**, 511 ; A. 1934, 937) determined the nuclear spin by hyperfine structure analysis, and this confirms the expectation that the mass number is odd.

Lines of the M-series of protoactinium were identified and tabulated by Pierce and Grosse, Physical Rev. 1935 [ii], **47**, 532, and the L-absorption constants by Dolejšek and Marek, Z. Physik, 1935, **97**, 70. M. C.

ACTINODAPHNINE *v.* *iso*QUINOLINE ALKALOIDS.

ACTINOLITE *v.* ASBESTOS.

ACTIVATED CARBON is essentially a al form of amorphous carbon deposited low temperature and free from adsorbed tabilised hydrocarbons which are normally iated with it (*v.* CHARCOAL, ACTIVE).

TIVIN, *Chloramin*, *Chloramine-T*, *Mia-* The sodium salt of *p*-toluene-sulpho- oroamide,

$$C_6H_4Me\cdot SO_2\cdot NClNa,3H_2O.$$

Colourless prisms. The anhydrous salt explodes at 175°–180°. Disinfectant and bleaching agent. A substitute for iodine in volumetric analysis (A. Noll, Chem.-Ztg. 1924, **48**, 845 ; J.C.S. 1925, A, ii, 66).

ACTOL. Trade name for silver lactate,

$$CH_3\cdot CH(OH)COOAg,H_2O.$$

Antiseptic.

ACTON. Trade name for ethyl orthoformate, $CH(OEt)_3$.

ACYLOINS. $\alpha\beta$-keto-alcohols. When aromatic aldehydes are heated with an alkali cyanide they condense to a compound of the type of benzoin :

$$2C_6H_5\cdot CHO = C_6H_5\cdot CO\cdot CH(OH)\cdot C_6H_5.$$

A mixture of aldehydes yields a mixed acyloin (Buck and Ide, J. Amer. Chem. Soc. 1930, **52**, 220, 4107). The mechanism of this reaction is doubtful (Lapworth, J.C.S. 1903, **83**, 995). The acyloins can also be obtained by the action of carbon monoxide on Grignard compounds (Egorova, J. Russ. Phys. Chem. Soc. 1914, **46**, 1319) :

$$\begin{aligned} 2CO+2MgRX &= 2O{:}CR\cdot MgX \\ &= MgX\cdot O\cdot CR(MgX)CR{:}O \\ &= OH\cdot CHR\cdot CR{:}O \end{aligned}$$

Aliphatic acyloins are best prepared by the action of sodium or potassium on ethereal solutions of aliphatic esters (Organic Syntheses, 1933, XIII, 26). They are among the products of the action of ferments, or of ultra-violet light, on various natural substances (Dirscherl, Z. physiol. Chem. 1931, **201**, 47, 78).

The acyloins display the properties of both ketones and alcohols. They form semicarbazones, which readily lose water giving anhydrobases (Henry and Paget, J.C.S. 1925, **127**, 1649). Their oximes form green copper compounds, insoluble in water but decomposed by acids (Feigl, Sicher, and Singer, Ber. 1925, **58** [B], 2294). The aromatic acyloins are oxidised by iodine to diketones (Corson and McAllister, J. Amer. Chem. Soc. 1929, **51**, 2822). The acyloins polymerise to dimerides and the simpler ones react with methyl alcohol and hydrochloric acid to form glucosidic *cyclo*acetals, which also polymerise easily.

Acetoin, $CH_3\cdot CH(OH)\cdot CO\cdot CH_3$, is prepared by reducing diacetyl with zinc and sulphuric acid, or by the action of ultra-violet light on acetaldehyde or pyruvic acid (Dirscherl, Z. physiol. Chem. 1930, **188**, 225). It is formed by the action of various enzymes on albumin (Cuisa, Annali Chim. Appl. 1932, **22**, 594, 747 ; A. 1932, 1987 ; 1933, 314). Acetoin has m.p. 15°, b.p. 140°–144°, d_4^{15} 1·0021, is miscible with water, readily soluble in alcohol and slightly so in ether. It polymerises on keeping to a dimeride of m.p. 95·5°, and in the presence of zinc to one of m.p. 85·5° (Diels and Stephen, Ber. 1907, **40**, 4338).

Acetol, $CH_3\cdot CO\cdot CH_2OH$, *q.v.*

Butyroin,

$$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)CO\cdot CH_2\cdot CH_2\cdot CH_3,$$

b.p. 180°–190°, 85°/10 mm., d_4^0 0·9367, $n_D^{16\cdot 7}$ 1·4355, is prepared by the action of finely divided sodium on ethyl-*n*-butyrate (Organic Syntheses, 1933, XIII, 24). The *oxime* has b.p. 143°/10 mm. ; the 2 : 4-*dinitrophenylhydrazone* has m.p. 99° (Allen, J. Amer. Chem. Soc. 1930, **52**, 2955). It is reduced to a mixture of the *meso*-form (m.p. 123°–124°) and the α-form ($[\alpha]_D^{23}$ +32° at least) of $\delta\epsilon$-octanediol by the action of bottom yeast (Veibel, Biochem. Z. 1931, **239**, 456).

Benzoin, $C_6H_5\cdot CO\cdot CH(OH)C_6H_5$, is a product of the reduction of benzoic acid or the oxidation of hydrobenzoin. It is usually prepared by the action of sodium cyanide on benzaldehyde (Organic Syntheses, 1932; Coll. vol. I, 88). It has been resolved into optically active forms by Wren (J.C.S. **1909**, **95**, 1583) and by Hopper and Wilson (J.C.S. 1928, 2483) ; it racemises readily. *dl-Benzoin* is a solid of m.p. 137°, slightly soluble in boiling water and in ether, soluble in hot alcohol. It is oxidised by Fehling's solution at room temperature to benzil. Like some other aromatic acyloins, it gives a reddish-purple colour with sodium methoxide solution (Corson and McAllister, J. Amer. Chem. Soc. 1929, **51**, 2822). It forms an *acetyl* compound of m.p. 82°–83° (Organic Syntheses, 1932, XII, 1). With thionyl chloride it gives *desyl chloride*,

$$C_6H_5\cdot CHCl\cdot CO\cdot C_6H_5$$

(*l.c.* 20). It condenses with urea to 4 : 5 diphenylglyoxalone (*l.c.* 34). The anti-*oxime* (α-oxime) has m.p. 151°–152°, the syn-*oxime* (β-oxime) m.p. 98°–99°. The α-oxime, *cupron* (*q.v.*)

is used analytically in the estimation of copper and molybdenum. The α-*phenylhydrazone* has m.p. 158°–159°, the β- m.p. 106° ; the *semicarbazone*, m.p. 206°. *l-Benzoin*, m.p. 131°–132·5°, has $[\alpha]_D^{12}$ −117·5° in acetone ; *acetate* $[\alpha]_D^{24}$ −217·7° in chloroform ; *oxime*, m.p. 164°, $[\alpha]_D^{24}$ −3·2° in chloroform. *d-Benzoin*, m.p. 131°–132·5°, $[\alpha]_D^{12}$ +120·5° in acetone (Wren, *l.c.*).

ADALINE, *Carbromal*, *Uradal*. α-bromo-α-ethylbutyrylcarbamide :

$$CBr(C_2H_5)_2CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m.p. 116°–118°. Slightly soluble in water. Sedative. For identification, *see* C. Genot (Chim. et Ind. 1925, **14**, 679 ; B. 1926, 75).

ADAMITE. A mineral consisting of hydrated basic zinc arsenate,

$$Zn_3(AsO_4)_2{\cdot}Zn(OH)_2,$$

discovered by C. Friedel in 1866 as a few small, violet orthorhombic crystals on silver ores from Chañarcillo in Chile. Since then it has been found at a few other localities, particularly in the ancient zinc mines at Laurion in Greece. Here it occurs in some abundance as bright green (cupriferous) or yellowish crystals in cavities of the cellular zinc ores. It has been prepared artificially in a crystalline condition.

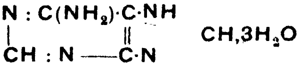
More recently the name *adamite* has been employed as a trade name for an artificial corundum manufactured for abrasive purposes.

L. J. S.

ADAMON, bornyl dibromodihydrocinnamate, $C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2C_{10}H_{17}$. Sedative.

ADANSONIA DIGITATA. The *baobab tree* (Fam. Bombacaceæ). A giant African tree, a girth of 112 ft. having been reported (Bull. Imp. Inst. 1923, **21**, 361). The soft wood and the bark have been used for paper making (*ibid.* 1920, **18**, 560) and the fibres of the inner bark for making ropes. For technical uses and bibliography, *cf.* K. Braun (Faserforschung, **8**, 90).

ADENINE, 6-*Aminopurine*,



$$\begin{array}{l} N : C(NH_2){\cdot}C{\cdot}NH \\ | \qquad\qquad\quad \| \qquad\qquad CH,3H_2O \\ CH : N \text{——} C{\cdot}N \end{array}$$

discovered in the pancreatic gland and spleen of the ox, occurs in all vegetable and animal tissues rich in cells (Kossel, Ber. 1885, **18**, 79, 1928 ; Z. physiol. Chem. 1886, **10**, 248 ; Yoshimura and Kania, Z. physiol. Chem. 1913, **88**, 351 ; Minuroto, J. Coll. Agric. Tokyo, 1912, **5**, 63 ; Smorodinzew, Z. physiol. Chem. 1912, **80**, 218 ; Zlataroff, Z. Nahr. Genussm. 1913, **26**, 242 ; Bass, Arch. exp. Path. Pharm. 1914, **76**, 40 ; Winterstein, Reuter, and Korolev, Landw. Versuchs-Stat. 1913, **79** and **80**, 541 ; Chapman, J.C.S. 1914, **105**, 1903) ; it has been extracted from tea leaves (Kossel, *l.c.*); from beet-juice (*v.* Lippmann, Ber. 1896, **29**, 2645); from beet-sugar residues (Andrlík, Z. Zuckerind. Böhm. 1910, **34**, 567), 0·05% pure adenine obtained from molasses (Stoltzenberg, Chem. Zentr. 1912, 1515, from Z. Ver. deut. Zucker-Ind. 1912, 318); from the young shoots of bamboo (Totani, Z. physiol. Chem. 1909, **62**, 113) ; from human excretory products (Krüger and Schittenhelm, Z. physiol. Chem. 1902, **35**, 159), and from herring brine (Isaac, Chem. Zentr. 1904, ii, 647, from Beitr. chem. physiol. Path. 1904, **5**, 500) ; it is one of the degradation products of nucleïn (Schindler, Z. physiol. Chem. 1889, **13**, 432), and is found in small quantity when nucleïn is heated with dilute sulphuric acid (Kossel, Ber. 1885, **18**, 1928 ; Jones and Richards, J. Biol. Chem. 1914, **17**, 71 ; 1915, **20**, 25).

Adenine has been found in the curative fraction of rice polishings (Drummond and Funk, Biochem. J. 1914, **8**, 598), but experiments with pure adenine sulphate do not reveal any vitamin B activity (Sure, *ibid.* 1933, **27**, 2043).

Adenine is isolated from tea extract, after the removal of caffeine, by precipitating the cuprous compound $C_5H_3N_5Cu_2$ by means of copper sulphate and sodium bisulphite, and decomposing the precipitate with ammonium sulphide ; the crude adenine is then isolated from the filtrate in the form of the sulphate. For the method of separating adenine from other purine bases compare Schindler (Z. physiol. Chem. 1889, **13**, 432). For recovery of adenine from the picrate, *see* Barnett and Jones (J. Biol. Chem. 1911, **9**, 93). The synthesis of adenine has been effected by reducing with hydriodic acid 6-amino-2 : 8-dichloropurine obtained by the action of aqueous ammonia on trichloropurine (E. Fischer, Ber. 1897, **30**, 2226 ; 1898, **31**, 104 ; Böhringer and Sons, D.R.P. 96927, 24/3, 97 ; Traube, Annalen, 1904, **331**, 64).

Adenine crystallises from dilute aqueous solution in long rhombic needles that become anhydrous at 110°, and melt with decomposition when rapidly heated to 360°–365° (Fischer, *l.c.*), and sublime in microscopic needles without decomposition at 220°. Adenine is sparingly soluble in cold (1 : 1086) and readily soluble in hot water (1 : 40) ; sparingly so in alcohol ; insoluble in ether or chloroform. It forms compounds with bases, acids and salts ; with hexose (Mandel and Dunham, J. Biol. Chem. 1912, xi, 85), and gives mono- and dichloroglucosides (Fischer and Helferich, Ber. 1914, **47**, 210). Adenine *d*-glucoside has m.p. 270°–275° (decomp.), $[\alpha]_D^{19°-20°}$ −10·5° in water, +5·67° in *N*-hydrochloric acid.

The *nitrate* $B{\cdot}HNO_3,\frac{1}{2}H_2O$ is crystalline, and the dry salt dissolves in 110·6 parts of water ; the *hydrochloride* $B{\cdot}HCl,\frac{1}{2}H_2O$ forms transparent monoclinic prisms $a : b : c = 2{\cdot}0794 : 1 : 1{\cdot}8127$, $\beta = 61° \, 40'$; the anhydrous salt dissolves in 41·9 parts of water ; the *chloroacetate* $C_5H_5N_5{\cdot}C_2H_3O_2Cl$ melts and decomposes at 162°–163° ; the *sulphate* $B_2{\cdot}H_2SO_4,2H_2O$, the *oxalate* $C_5H_5N_5{\cdot}C_2H_2O_4,H_2O$, and *dichromate* $(C_5H_5N_5)_2{\cdot}H_2Cr_2O_7$ are crystalline ; the *picrate* $C_5H_5N_5{\cdot}C_6H_3N_3O_7$ is stable at 220°, and is so sparingly soluble in cold water (1 : 3500) that it is used as a means of estimating adenine in solution (Ber. 1890, **23**, 225) ; the addition of sodium picrate will precipitate adenine from exceedingly dilute solutions (1 : 13,000) (Barnett and Jones, *l.c.*) ; the *picrolonate* $C_5H_5N_5{\cdot}C_{10}H_8O_5N_4$ crystallises from water and melts at 265° (Levene, Biochem. Z. 1907, **4**, 320). The *platinichloride*, $B_2{\cdot}H_2PtCl_6$, crystallises from dilute solution in needles, and yields the *salt* $C_5H_5N_5 \cdot HCl \cdot PtCl_4$ when a concentrated solution is boiled. The *acetyl* derivative $C_5H_4N_5Ac$ does not melt at 260°, the *benzoyl* derivative $C_5H_4N_5Bz$ has m.p. 234°–235° (Kossel, Ber. 1886, **20**, 3356). The *methyl* and *benzyl* derivatives have been prepared (Thoiss, Z. physiol. Chem. 1889, **13**, 395). *Bromoadenine* $C_5H_4N_5Br$ is strongly basic, forms an insoluble *picrate*, and on oxidation with hydrochloric acid and potassium chlorate yields alloxan, urea and oxalic acid (Bruhns, Ber. 1890, **23**, 225 ; Krüger, Z. physiol. Chem. 1892, **16**, 329). Adenine is converted into hypoxanthine by the action of nitrous acid (Kossel, Ber. 1885, **18**, 1928). Adenine-*d*-glucoside treated with excess of nitrous acid yields hypoxanthine-*d*-glucoside, m.p. 245°, $[\alpha]_D^{20°} -34{\cdot}5°$ in *N*-soda, $+12{\cdot}92°$ in *N*-hydrochloric acid (Fischer and Helferich, *l.c.*).

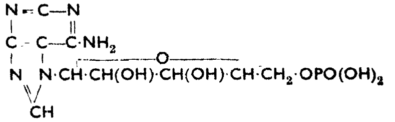
Adenine-uracil-dinucleotide is obtained as an amorphous powder by the action of dilute ammonium hydroxide on yeast-nucleic acid ; it has $[\alpha]_D\ -6{\cdot}8°$, and gives a crystalline brucine salt, $C_{19}H_{25}O_{15}N_7P_2 \cdot 4C_{23}H_{26}O_4N_2,14H_2O$, m.p. 174°–175° (decomp.).

Methods for the estimation of adenine are given by Schmidt (Z. physiol. Chem. 1933, **219** 191), and Jorpes (Biochem. J. 1934, **28**, 2012).

M. A. W. and W. V. T.

ADENOS. Trade name for fine Oriental cotton.

ADENOSIN is a nucleoside, formed by condensation of adenine and the pentose *d*-ribose. *Adenylic acid* is a nucleotide, the monophosphoric acid of adenosin,



Yeast adenylic acid is adenosin-3-phosphoric acid.

ADHESIVES AND ADHESIVE ACTION. The old idea that only substances of a gelatinous character had adhesive properties has long been discarded ; McBain and Lee (Proc. Roy. Soc., A., 1927, **113**, 606) found that strong joints can be obtained with any liquid material which could " wet " both the surfaces to be joined and which could be solidified *in situ*. Water (after freezing), sulphur (molten and subsequently cooled), oleic acid (after freezing), pure coumarin and other pure chemical compounds could all produce strong joints, the adhesive strength of such substances varying in definite relation to chemical constitution.

There is, indeed, a close connection between adhesion and the architecture of the molecule, both in the case of pure liquids and pure solids. It may be said that, in general, aromatic compounds tend to give stronger joints than aliphatic compounds. Straight chain compounds are all poor adhesives while, on the other hand, such substances as coumarin, triphenyl carbinol, aurin, rosolic acid and many more show strong adhesive properties.

There are two types of adhesion : the true or specific adhesion, and the mechanical adhesion. When two highly polished metal surfaces or surfaces of optically polished glass are placed in contact we have true adhesion ; when the two surfaces are more or less porous (wood, unglazed porcelain, paper, etc.) the adhesion is mechanical and due to mechanical embedding of an adhesive in the pores of the material to be joined. Whatever the nature of the adhesive used and the surfaces to be joined, strength and other properties of the joint depend on the properties of the film of adhesive between the two surfaces. The strength of the joint depends on the strength of the film, as through the latter stresses are transmitted to the surfaces ; but it is also essential that the film should have elasticity, flexibility and ductility (deformability). The lack of deformability will lower the value of an adhesive, if it cannot adapt itself to changes in shape and volume when the joint is " setting " or drying, or when the conditions of the joint are changed owing to changing atmospheric conditions.

The strength of a joint is also dependent on the thickness of the adhesive film. The thinnest films yield the best results ; the strength increasing very rapidly when the adhesive layer is reduced ; measurements carried out by McBain and Lee (J. Physical Chem. 1927, **31**, 1674) have shown the greatest effect is noticeable in layers less than one-millionth of an inch thick.

Adhesives are varied in chemical character and their applications are equally varied. Glue (*q.v.*) is the typical adhesive, but there are a large number of compounds which, because of special properties, are more suitable for certain specific purposes.

Cellulose esters and ethers are now very widely used in many industries, especially when a high resistance to moisture together with a good adhesive strength is necessary. In the manufacture of leather belting they have found extensive application. For use they are dissolved in suitable solvents, such as amylacetate for celluloid or nitro-cotton, acetone for cellulose acetate, benzene or its higher homologues for benzyl cellulose.

Resins, natural or artificial, form cements which give the best results for joints between metal surfaces. Recent developments in the manufacture of artificial resins and in the methods of applying them as adhesives make possible the practical use of " thermosetting " resins in the manufacture of plywood. This is possible by suspending the finely powdered resin in water in the presence of a suitable protective colloid. The suspension is spread on the surface to be joined, and the water, used as a vehicle, allowed to evaporate. Upon drying the resin adheres to the wood surfaces to be joined ; when heat and pressure are applied the resin will soften and obtain a hold on the wood ; by further application of heat it will harden to an infusible insoluble mass joining the two surfaces.

Gums, and especially those from the " Acacias " (gum arabic), form the basis of many adhesives used in the paper trade. Those from Kordofan, Gedda and Senegal are highly valued.

Casein, a protein from milk, has been used in very large quantities during recent years, and especially during the Great War period, because of its property of forming a waterproof adhesive. Casein is obtained by coagulating the caseinogen of skimmed milk, either by acids or by means of rennin (rennet), the latter giving a product more suitable for adhesive purposes. Casein cements are prepared by dissolving the protein in alkali or in salts solutions, especially sodium salts ; if a waterproof adhesive is desired, the addition of a suitable amount of slaked lime is necessary. The waterproof property of the resulting cement is probably due to the formation of an insoluble calcium salt.

Blood cements are prepared by treating either fresh defibrinated blood or dry " blood albumin," dissolved in water, with ammonia and slaked lime : the addition of a filler is advisable in order to give the mixture a suitable consistency. These cements which will not "set" at ordinary temperature do so at a temperature of 50°-60°, and are extensively used in the manufacture of plywood.

Starches and Dextrins.—Very few adhesives have found such wide applications as starch adhesives. Their relatively low cost is an important advantage and has stimulated their application in many manufacturing processes in which ordinary glues were originally used. Starches of different origin vary widely in their adhesive properties, which are considerably modified by the presence or absence of certain products, *e.g.* hemicellulose.

Alexander (" Colloid Chemistry," New York, 1927) has shown that highly aggregated raw starches are not as good adhesives as those which have been subjected to a partial degradation, the products possessing the most powerful adhesive action being those which lie near, but not quite in, the zone of true or crystalloidal solutions. For example, dextrins and alkali starches are better adhesives than pure starch on the one hand, or dextrose, the final degradation product, on the other ; the maximum adhesiveness seems to correspond to the zone of maximum colloidal character.

The wide varieties of starch adhesives and sizing materials may be, for simplicity, classified under several headings : (1) Pastes made by simply boiling starch with water, suitable for laundry work or for sizing textiles. (2) Starches treated with alkali : the starch is made into a thin milk and the alkali is slowly run in with constant stirring ; the starch granules will swell and burst into a clear jelly giving an adhesive of considerable strength. Cassava starch gives the best results. Such an adhesive is used for making wood or cardboard boxes, and it is specially suitable for use in gluing machines as it has no tendency to froth. It cannot, however be used for veneering as the alkali would stain the veneers. (3) Starches treated with acids, especially sulphuric acid, the treatment being followed by neutralisation of the acid. These adhesives can be dried and stored as a powder: they are used by paper-hangers. (4) Starches may also be treated with concentrated solutions of certain salts which have the effect of " gelatinising " the starch granules. The chlorides of Ca, Mg, or Zn are the most commonly used for the preparation of pastes so extensively employed in office work.

The *dextrins* are prepared by the action of heat, acids or diastase on starches, and their properties depend on those of the particular starch used as raw material. They are known by various names (*vegetable gum, starch gum, gommaline, British gum,* etc.), and form yellowish or brown powders, the colour depending on the purity of the product and the method of preparation. Dextrins are soluble in water and can be used as adhesives without the addition of alkali or salts. When dry they give a brittle film : the addition of certain salts (*e.g.* sodium or ammonium phosphate) renders the film more elastic. Potato starch gives the best dextrin. Dextrin cements find application in many industries and especially for making envelopes.

References.—Reports of the Adhesives Research Committee (London, H.M.S.O. 1922, 1926, and 1932).

For more detailed information on casein and the use of cellulose esters and ethers the reader may consult Scherer, " Casein " (Scott, Ringwood, London), and Worden, " Technology of Cellulose Esters " (*see also* CASEIN).

Valuable information on starches and dextrins is to be found in Walton, " A Comprehensive Survey of Starch Chemistry " (New York, 1928) and in J. Alexander, " Colloid Chemistry " (New York, 1927) J. C. K.

ADIPIC ACID. Butane-$\alpha\delta$-dicarboxylic acid, $CO_2H\cdot[CH_2]_4\cdot CO_2H$, occurs in beet juice. It can be obtained by oxidising with nitric acid the fraction from Russian petroleum boiling at 78°–82° (Aschan, Ber. 1899, **32**, 1769) ; by oxidising sebacic acid and various fats with nitric acid ; by heating β-iodopropionic acid with silver, or by the reduction of mucic, muconic, saccharic or *iso*-saccharic acids. It is most conveniently prepared by oxidising *cyclo*hexanol with nitric acid (Kon and Thorpe, Organic Syntheses, 1925, **5**, 9 ; U.S.P. 1921101, 1960211) or by oxidising *cyclo*hexanone with alkaline permanganate (Rosenlew, Ber. 1906, **36**, 2202 ; Mannich and Hancu, Ber. 1908, **38**, 575).

The acid crystallises in monoclinic laminæ, m.p. 153°–153·1° (Serwy, Bull. Soc. chim. Belg. 1933, **42**, 483), subliming at a more elevated temperature ; although only slightly soluble in water it exhibits a marked tendency to form supersaturated solutions ; it is readily soluble in hot alcohol and in ether. For values of its dissociation constant, *see* Böeseken and Verkade (Rec. trav. chim. 1917, **36**, 170), Kolthoff and Bosch (*ibid.* 1928, **47**, 861), Gane and Ingold (J.C.S. 1928, 1598).

Adipic acid is conveniently characterised as its *phenacyl ester*, m.p. 87·6°, or its p-*bromophenacyl ester*, m.p. 154·5° (Kelly and Kleff, J. Amer. Chem. Soc. 1932, **54**, 4444).

Salts.—Adipic acid forms crystalline metallic salts which are generally water-soluble ; distillation of calcium adipate yields *cyclo*pentanone.

Esters.—Electrolysis of potassium ethyl succinate yields *diethyl adipate*, b.p. 131°/13 mm.; *dipropyl adipate*, b.p. 155°/16 mm., and *di*-n-*butyl adipate*, b.p. 145°/4 mm. are obtained by ordinary methods of esterification. Of the acid esters *ethyl hydrogen adipate* has m.p. 29°, b.p. 160°/7 mm., the n-*propyl hydrogen ester* b.p. 146°/14 mm., and the n-*butyl hydrogen ester* b.p. 155·5°/4 mm. For physical constants of the diethyl ester, *see* Serwy (*l.c.*), Sakurada and Taniguchi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **20**, Abstracts 404–408) and Vogel (J.C.S. 1934, 333).

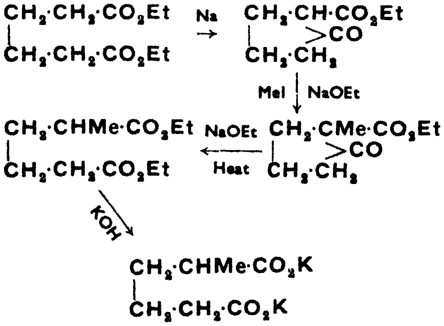
Adipyl dichloride, b.p. 125°–128°/11 mm., is obtained from adipic acid and thionyl chloride; the *diamide* has m.p. 222°, and the *dinitrile*, obtained from tetramethylene dibromide and potassium cyanide, is a low melting solid, m.p. 1°, b.p. 295°.

Adipodialdehyde is a liquid, m.p. −7° to −8°, obtained by oxidising *cyclo*hexene with lead tetracetate or by catalytic reduction of *cyclo*hexene ozonide (Criegee, Annalen, 1930, **481**, 263; Fischer and others, Ber. 1932, **65** [B], 1467; 1933, **66** [B], 665); it forms a diphenylhydrazone, m.p. 140°, and a dioxime, m.p. 184°.

Adipic anhydride.—A monomolecular anhydride, m.p. 97°, may be obtained by boiling adipic acid with acetic anhydride. It readily polymerises, the product undergoing partial depolymerisation on heating *in vacuo*, but the distillate reverts rapidly to the polymeride. Substitution by methyl groups increases the stability of the monomeric anhydride, the *anhydride*, m.p. 189°, of *βββ′β′-tetramethyl adipic acid* gives a cyclic ketone, b.p. 186°–189° (*semicarbazone*, m.p. 223°) on heating, but the anhydride, m.p. 166°, of *ααα′α′-tetramethyl adipic acid* does not do so, and furthermore, is stable towards water and alkali (Farmer and Kracovski, J.C.S. 1927, 680).

For the *α-halogenoadipic acids* and their esters, *see* Ingold (J.C.S. 1921, 961), and for the *di-* and *tetrahalogeno* derivatives, *see* Ingold (*l.c.*), Perkin and Robinson (J.C.S. 1921, 1392); Bernton, Ing, and Perkin (*ibid.* 1924, 1492), and Farmer (*ibid*, 1923, 2539): for *dihydroxyadipic acid*, *see* Freudenberg, Bruce, and Gauf (Annalen, 1934, **510**, 206).

Alkyl and Aryl Adipic Acids.—In general the substituted adipic acids are obtained by oxidising the appropriately substituted *cyclo*hexanol or *cyclo*hexanone. The α-alkyl and αα′-dialkyl adipic acids may also be prepared by alkylating the ·CH· group in the β-keto-*cyclo*pentancarboxylic ester produced by the action of sodium or sodamide on adipic ester, the ring being subsequently reopened by boiling with alcoholic sodium ethoxide:



The following are described: *α-methyladipic acid*, m.p. 64° (Bouveault and Locquin, Bull. Soc. chim. 1908 [iv], **3**, 436, 450; Dieckmann, Annalen, 1901, **317**, 69; Markownikoff, *ibid.* 1904, **336**, 302); *β-methyladipic acid*, m.p. 94° (Sabatier and Mailhe, Compt. rend. 1871, **158**, 988; Juery, Bull. Soc. chim. 1915 [iv], **17**, 173; Markownikoff, *l.c.*). Ciamician and Silber (Ber. 1913, **46**, 3080) record the m.p. as 97°; *αα-* and *αα′-dimethyladipic acids* (Meerwein and Unkel, Annalen, 1912, **376**, 161; Noyes and Kyriakides, J. Amer. Chem. Soc. 1910, **32**, 1061); *α-phenyladipic acid*, m.p. 132°–133° (Case, *ibid.* 1933, **55**, 2927) and β-benzoyladipic acid, m.p. 110°–111°, which gives the corresponding anhydride, m.p. 90°, on distillation (*v.* Braun, Bayer, and Cassel, Ber. 1927, **60** [B], 2602). G. F. B.

ADIPOCERE (from *adeps*, fat, and *cera*, wax). A peculiar waxy substance which is frequently formed as a product of the decomposition of human or mammalian corpses which have been buried in wet soil (*cf.* Müller, Arch. Hyg. 1914, **83**, 285). It was first observed by Fourcroy in 1786, when the bodies were removed from the Cimetière des Innocents in Paris: a large number of coffins had remained piled together for many years, and in many of these the corpses had been converted into a saponaceous, whitish substance, which Fourcroy placed, together with spermaceti and cholesterol in a special class termed *adipocere*. Chevreul, however, clearly differentiated the three substances, and was able to show that corpse adipocere (*gras*) consisted chiefly of free fatty acids with small amounts of lime soaps and minor quantities of mineral salts and nitrogenous decomposition products of the body tissues (M. E. Chevreul, “Les Corps gras d'Origine animale,” 1923).

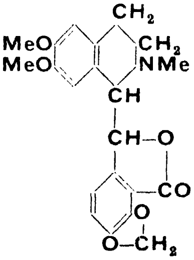
Gregory (Annalen, 1847, **61**, 362) expressed the view that the fatty acids had been formed by the hydrolysis of the body-fat, all the glycerol simultaneously liberated having been washed away, with other soluble matters, by percolating water. Similarly Strassmann and Fantl (Deut. Z. ges. gerichtl. Med. 1925, **6**, 168) and Ruttan (Trans. Roy. Soc. Canada, 1916 (iii), **10**, Sec. III. 169; *cf.* Ruttan and Marshall, J. Biol. Chem. 1917, **29**, 319; Goy, Biochem. Z. 1927, **187**, 470), conclude that adipocere results from the slow hydrolysis and oxidation[1] of the body-fat; the part, if any, played by micro-organisms (bacteria, etc.) in these changes is, however, still obscure (*cf.* Ruttan, *l.c.*; A. Tschirch and Gfeller, Chem. Umschau, 1925, **32**, 181). The suggestion put forward by Krattan and by Bianchini (Biochem. e. terap. sperim. 1925, **12**, 16; *cf.* Remy, Arch. Hyg. 1926, **96**, 311; Issoglio, Giorn. farm. chim. 1916, **65**, 361) that all or some of the fatty acids of adipocere may arise from the decomposition of albuminous constituents of the body is opposed by Strassmann and Fantl on the ground that the fatty acids, if derived from such sources, would possess a lower molecular weight than is actually the case. The metallic soaps present are evidently formed by the action of fatty acids on the lime and magnesium salts present in or derived from other body-tissues, such as the bones.

---

[1] Some cases of extraordinarily rapid formation of adipocere in the tropics are recorded by Taylor (Medical Jurisprudence, 1920 ed., Vol. II.).

Adipocere contains from 70–98% of ether-soluble material, 0–5% of ash (mainly **CaO** and **MgO**), with traces of nitrogenous and other impurities. The constituent fatty acids, which have a much lower iodine value than the body-fats from which they were formed, include stearic and palmitic acids, and are particularly characterised by the presence of the isomeric 9- and 10-hydroxystearic acids corresponding to the hydroxylation of oleic acid. Varying amounts of unsaturated acids (oleic acid) may be present in specimens of the soft, oily, "immature" adipocere, in which the decomposition is not far advanced. According to Ruttan, the final stage in the formation of "mature" adipocere is characterised by the absence of glycerides and the complete disappearance of oleic acid by conversion into hydroxystearic acids. E. L.

ADLUMINE, $C_{21}H_{21}O_6N$, is an alkaloid, m.p. 180°, having the structure,



It is associated with *adlumidine*,

$$C_{19}H_{15-17}O_6N,$$

m.p. 235, in *Adlumia fungosa* Greene (Manske, Canad. J. Res. 1933, **8**, 210, 404), and has only a weak convulsant action (Welch and Henderson, J. Pharm. Exp. Ther. 1934, **51**, 482). The alkaloid, $C_{30}H_{29}O_9N$, m.p. 188°, which was isolated from *A. cirrhosa* by Schlotterbeck and Watkins (Pharm. Arch. 1903, **6**, 17) and termed "adlumine" may be an impure isomer of bicuculline.

ADMIRALTY GUN-METAL. No. 1, an alloy of 88 parts copper, 10 tin and 2 zinc, used for steam valves. No. 2a, 88 copper, 13 tin, 1 zinc; resists high-pressure water, used for gun mountings.

ADMIRALTY WHITE METAL for bearings. Tin alloy containing 8–9% antimony and 3–7% copper.

ADNIC. An alloy of 70 copper, 29 nickel, and 1 tin, extensively used for condenser tubes, steam traps and apparatus intended to resist brine, hot caustic soda and organic acids. For these purposes it is generally superior to pure nickel (W. B. Price, Met. & Alloys, 1934, **5**, 71, 77; Ann. Report Soc. Chem. Ind. 1934, 377; B. 1934, 503).

ADONIS VERNALIS (Fam. Ranunculaceæ). Pheasants Eye. The drug is the dry herb, resembling digitalis in its action. It contains the glucoside adonin, $C_{24}H_{40}O_9$, the sugar alcohol adonitol, $C_5H_7(OH)_5$, choline, phytosterin, $C_{27}H_{46}O$, m.p. 138°–139,° phytosterolin, $C_{33}H_{56}O_6$, and a very small quantity of 2 : 6 dimethoxy-*p*-benzoquinone. Two highly active digitalis-like glucosides are also present according to K. Fromherz (Münch. med. Woch. 1928, **75**, 818; Chem. Zentr. 1928, ii, 75). For the manufacture of a cardio-active glucoside, *see* F. Hoffmann-La Roche A.-G. (B.P. 265941, Conv. 13.2.26; B. 1927, 797; B.P. 288129, Ger. Appl. 1.4.27; B. 1928, 874).

ADONITOL, $C_5H_{12}O_5$, m.p. 102°, optically inactive, is the alcohol corresponding to the riboses and is obtained from them on reduction. It is found in *Adonis vernalis*; the leaves of which are able to convert adonitol into starch but can make use of no other carbohydrate alcohols. It forms a *dibenzylidene derivative*, m.p. 164°. E. F. A.

ADRENALINE. *Adrenalina B.P.*, *Epinephrina U.S.P.*, *Epinephrine*, *Suprarenin*, *l-a-3 : 4-dihydroxyphenyl-β-methylaminoethanol*,

$$C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NH \cdot CH_3.$$

A "chromogen," coloured green by ferric chloride and rose-red by iodine, was discovered in the suprarenal medulla by Vulpian (Compt. rend. 1856, **43**, 663), but the remarkable rise of blood pressure caused by intravenous injection of suprarenal gland extracts was not observed until 1894 (Oliver and Schäfer, J. Physiol. 1894, **16**, i). After numerous attempts the active principle, which turned out to be also the chromogen, was first obtained crystalline by Takamine (Eng. Pat. 1467, 1901; J.S.C.I. 1901, **20**, 746), and almost simultaneously by Aldrich (Amer. J. Physiol. 1901, **5**, 457). The constitution was next established, mainly by Pauly (Ber. 1903, **36**, 2944; 1904, **37**, 1388) and by Jowett (Trans. Chem. Soc. 1904, **85**, 192). The racemic substance was synthesised by Stolz (Ber. 1904, **37**, 4149; and D.R.P. 152814, 157300 of Farbw. Meister, Lucius, und Brüning; *cf.* also Dakin, Proc. Roy. Soc., B. 1905, **76**, 491). As the racemic substance was found to have little more than half the activity of the natural lævo-variety, its resolution was effected by Flächer (Z. physiol. Chem. 1908, **58**, 581; and D.R.P. 222451). The synthetic *l*-base thus obtained is identical with the natural active principle.

The name *epinephrine* was first applied by Abel to **N**-benzoyl adrenaline, but later to the active substance itself, and it is under this name that the substance is referred to in the U.S.P., for instance. The objection to adrenaline is that it is a trade name; close on thirty other trade names have been in use for the substance.

Preparation of the natural substance.—The minced glands (generally of oxen) are extracted with dilute acid at 90°–100°; the extract is evaporated to a small bulk, purified with neutral lead acetate, and finally precipitated with several volumes of ethyl or methyl alcohol. The alcoholic filtrate, after concentration to a small bulk, is precipitated with excess of *concentrated* ammonia, when the adrenaline crystallises in sphærites on standing. Oxidation must be guarded against as far as possible, by boiling with zinc dust, or by extracting with water containing sulphur dioxide; the evaporation is conducted *in vacuo* in a carbon dioxide atmosphere and the precipitation by ammonia takes place under a layer of petrol (Takamine, *l.c.*; Aldrich, *l.c.*; von Fürth, Monatsh. 1903, **24**, 261). Abel (Ber. 1903, **36**, 1839) extracts at once with a 3·5% alcoholic solution of trichloracetic acid, which eliminates further purification, and seems to give a good yield. Bertrand (Bull. Soc. chim. 1904 [iii], **31**, 1289) extracts with 95% alcohol containing oxalic acid, evaporates, shakes with petrol, and purifies with lead acetate.

The crude sandy adrenaline contains inorganic matter, and may be purified by solution in acid and reprecipitation, but better by utilising the solubility of the oxalate in alcohol ; the crude base is ground up with a 15% solution of oxalic acid in 85–90% alcohol, which leaves inorganic impurities behind (Abel, Pauly).

Syntheses.—Catechol is condensed with monochloracetic acid, by means of phosphorus oxychloride, and the resulting chloroacetocatechol (3 : 4-dihydroxy-ω-chloroacetophenone),

$$(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2Cl,$$

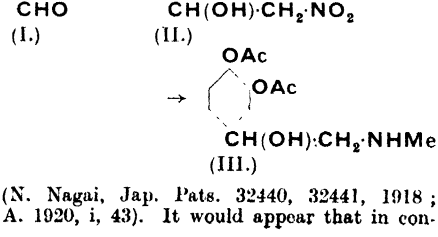
is suspended in alcohol (50 c.c. for 100 grms. of the ketone) ; 200 c.c. of a 40% aqueous methylamine solution are added ; on standing methylaminoaceto catechol,

$$(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CH_3,$$

separates out, and is washed with water, alcohol, and ether. The ketone is then reduced to the secondary alcohol by aluminium amalgam, or catalytically. For the resolution the bitartrate is extracted with methyl alcohol ; *d*-adrenaline-*d*-tartrate dissolves and *l*-adrenaline-*d*-tartrate remains behind. The *d* adrenaline so obtained is also utilised, for it may be racemised by heating with dilute hydrochloric acid, and converted into the crystalline racemic hydrochloride (D.R.P. 220355), which can then be resolved.

The synthesis from chloroacetocatechol appears to be the only one of practical importance, but various others have been described, for which the following may be consulted : Mannich, Arch. Pharm. 1910, **248**, 127 ; German patents 155632, 185598, 189483, 193634, 195814, 209609, 209610, 209962, 212206, 216640 ; Friedländer, viii, 1181–1190 ; ix, 1024–1033.

The most recent synthesis is a modification of some earlier ones. Diacetylprotocatechuic aldehyde (I) on condensation with nitromethane in feebly alkaline aqueous solution yields β-hydroxy-β-3 : 4-diacetoxyphenylnitroethane (II). When this is mixed with the calculated quantity of formaldehyde and reduced by zinc and acetic acid, β-hydroxy-β-3 : 4-diacetoxyphenyl ethyl methylamine (III) is formed, from which adrenaline is obtained on removal of the acetyl groups :



(I.) (II.) (III.)

(N. Nagai, Jap. Pats. 32440, 32441, 1918 ; A. 1920, i, 43). It would appear that in connection with the great slaughter-houses in the U.S.A. natural adrenaline can be produced more cheaply there than the resolved synthetic product in Europe.

Properties.—Natural adrenaline, when pure, forms colourless sphæro-crystals, m.p. 211°–212°, $[\alpha]_D$ −53° ; the solubility in water at 20° is 0·0268%, and it is also very slight in most organic solvents. Racemic adrenaline decomposes at 230°. Adrenaline dissolves in the calculated quantity of mineral acids, or even in slightly less ; it also dissolves in caustic alkalis. Its chief chemical characteristic is the ease with which it undergoes oxidation (*see* Colour reactions, below). Solutions with a slight excess of acid are the most stable ; traces of iron accelerate oxidation (Gunn and Harrison, Pharm. J. 1908 [iv], **26**, 513).

The salts of the optically active adrenalines are mostly amorphous and deliquescent ; the *borate* is relatively stable (D.R.P. 167317). The chief crystalline salt is the *bitartrate* employed in the resolution of the racemic base. The latter yields a crystalline *hydrochloride*, m.p. 157° (D.R.P. 202169), and a crystalline *oxalate* ; the corresponding optically active salts are amorphous.

Colour reactions. Colorimetric estimation.—There are three kinds of colour reactions for adrenaline : (1) the general catechol reaction with ferric chloride (limit of green coloration 1 : 30,000) ; (2) the phosphotungstic reaction of Folin, Cannon, and Denis (J. Biol. Chem. 1913, **13**, 477 ; *cf.* Folin and Denis, *ibid.* 1912, **12**, 239), in which the reagent gives a highly coloured blue reduction product ; (3) a reaction with a considerable number of mild oxidising reagents, in which the adrenaline is converted into apparently one and the same rose-red oxidation product. For the colorimetric estimation of pure adrenaline solutions the reaction of Folin, Cannon and Denis is the most suitable, and agrees closely with physiological measurements (Seidell, J. Biol. Chem. 1913, **15**, 197 ; Johannessohn, Biochem. Z. 1916, **76**, 377). The reagent employed is the same as for the estimation of uric acid, but adrenaline is three times as sensitive (Johannessohn gives the ratio 2·98. Autenrieth and Quantmeyer (Münch. med. Wochenschr. 1920, **68**, 1007) give it as 3·3). To prepare the phosphotungstate reagent 100 g. sodium tungstate are dissolved in 750 c.c. of water, 80 c.c. of 85% (syrupy) phosphoric acid added, the solution is boiled gently for 1½–2 hours and then made up to 1 litre ; $\frac{1}{300}$–$\frac{1}{400}$ mg. adrenaline can be detected ; limit 1 : 3,000,000. The blue colour soon fades. Uric acid solutions are used as standards.

For the estimation of adrenaline in extracts of the gland which are always more or less yellow in colour, the phosphotungstate reagent is less suitable (Seidell, *l.c.*). Maiweg (Biochem. Z. 1922, **134**, 292) finds that with partially decomposed solutions the Folin-Denis reagent gives higher values than the blood-pressure test. He passed air through solutions of adrenaline at 38° and p_H 7·35 :

Average values after	0	1	2	3	4 hrs.
Folin, Cannon, and Denis	100	75	35	33	25%
Blood pressure . .	100	55	27·5	12·5	6%

Incidentally, this table gives some idea of the instability of neutral solutions. At p_H4 air can be passed for hours without appreciable loss. Johannessohn (*l.c.*) found that good commercial preparations lost half their activity in 3½ years, and two-thirds in 4¾ years.

The Folin-Denis reagent is also unsuitable for mixtures of adrenaline with cocaine, novocaine, etc., because the latter bases are precipitated by the reagent (Johannessohn, *l.c.*). In these cases a reaction of the third type seems preferable (3). Seidell shakes 10 c.c. of gland extracts containing 1 : 50,000 adrenaline for 1 hour with 5 mg. of powdered manganese dioxide, filters, and matches the colour with that of standards, prepared by mixing, in various proportions, a solution of 2 grms. $CoCl_2 \cdot 6H_2O$+1 c.c. concentrated hydrochloric acid in 100 c.c. water, with an auric chloride solution containing 0·1 grm. $AuCl_3$ in 100 c.c. water. These mixtures are standardised by comparison with a 1 : 100,000 solution of pure adrenaline, mixed with an extract of desiccated thyroid gland (which has the same yellow colour as a suprarenal extract).

For mixtures containing cocaine, etc., Johannessohn employs the Fränkel-Allers reaction (Biochem. Z. 1909, **18**, 40), which consists in adding an equal volume of 0·001 *N*-potassium *bi*-iodate and a few drops of phosphoric acid, and heating nearly to the boiling-point ; a red colour is obtained with adrenaline up to 1 : 100,000 or 1 : 300,000 (*cf.* Scoville, Ind. Eng. Chem. 1920, **12**, 769). Other oxidising reagents giving a red colour are auric chloride (Gautier, Compt. rend. Soc. de Biol. 1912, **73**, 564 ; very delicate), potassium persulphate (Ewins, J. Physiol. 1910, **40**, 317 ; 1 : 5,000,000), iodine, mercuric chloride, potassium ferricyanide, bromine, bleaching powder, osmic acid. For a detailed criticism of the quantitative application of these reagents, *see* Borberg (Skand, Arch. Physiol. 1912, **27**, 341), also Bayer (Biochem. Z. 1909, **20**, 178) for means of making them more sensitive but less specific.

Physiological methods of estimating adrenaline are more reliable and more accurate than the colorimetric. The blood pressure of a cat, with brain and spinal cord destroyed, and without anæsthetic reacts, according to Elliott (J. Physiol. 1912, **44**, 374), " with mechanical accuracy," and permits of the estimation of the adrenaline content of a cat's suprarenal with an error of 0·01 mg. (3–4% of the total amount present). Since the expiration of the German patent of 1903, a number of synthetic preparations have appeared on the market, which are wholly or partly racemic ; the necessity of their control by physiological means has been pointed out by Tiffeneau (J. Pharm. Chim. 1921, **23**, 313, 366).

Fresh bullock's suprarenals may contain up to 0·25% adrenaline. A fresh bullock's gland dissected free from fat weighs about 10–12 grms. The actual yield in manufacture often does not exceed 0·1% from bullock's glands ; sheep, and especially hogs, contain less. The dried secretion of the parotid gland of *Bufo agua*, a Central American toad, contains as much as 5% of adrenaline (Abel and Macht, J. Pharm. Exp. Ther. 1912, **3**, 319).

The most important *physiological action* of adrenaline is that on the arterioles, causing constriction and rise of blood pressure. Intravenously minute doses (0·0003 mg. per kilo. in rabbits) produce a distinct effect. Applied to a mucous surface, it causes marked local vaso-constriction and blanching ; on this property depends its chief use as a hæmostatic in surgery. It is often used mixed with a local anæsthetic like cocaine. Most commercial solutions and the *Liquor adrenalini hydrochloricus* of the B.P. contain 0·1% adrenaline dissolved in a slight excess of acid (*e.g.* one-half equivalent) which renders them more stable than solid tablets (according to Johannessohn, *l.c.* ; Gunn and Harrison, *l.c.*). Chloroform (B.P.) or other preservative may be added, and salt to make the solution isotonic with the blood. For sterilisation by heat, *see* Rowe (Amer. J. Pharm. 1914, **86**, 145). Adrenaline has been recommended (in oral doses of 5–6 mg. per 24 hours) for sea-sickness (Revue Scientifique, 1917). The physiological activity of *d*-adrenaline is about $\frac{1}{15}$ of that of *l*-adrenaline (*e.g.* Cushny, J. Physiol. 1909, **38**, 259 ; Tiffeneau, Compt. rend. 1915, **161**, 36), and hence the racemic base is slightly more than half as active as the natural variety.

Adrenaline substitutes.—Numerous amines have an action more or less resembling that of adrenaline (Barger and Dale, J. Physiol. 1910, **41**, 19). Three, all closely related to adrenaline in structure, have been recommended as substitutes, but have not found wide application. Racemic *arterenol*, 3 : 4-dihydroxyphenylethanolamine $(OH)_2C_6H_3 \cdot CH(OH) \cdot CH_2 \cdot NH_2$ (*see* above), m.p. 191° (hydrochloride, m.p. 141°), is said to be about half as active as *l*-adrenaline. *Homorenon*, ω-ethylamino-3 : 4-dihydroxyacetophenone $(OH)_2C_6H_3 \cdot CO \cdot CH_2 \cdot NH \cdot C_2H_5$ forms a crystalline hydrochloride, m.p. 260°, and has a very much weaker action than adrenaline. *Epinine*, 3 : 4-dihydroxyphenylethylmethylamine $(OH)_2C_6H_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_3$, m.p. 188°–189° (Pyman, Trans. Chem. Soc. 1910, **97**, 272), is intermediate in action between the two former bases. (For Tyramine, *see* article on ERGOT.)

For a more detailed account of the chemical and physiological properties of adrenaline, *see* Barger, " The Simpler Natural Bases," Longmans, 1914, pp. 81–105 ; Guggenheim, " Die biogenen Amine," Berlin, 1924 ; Barger, " Some Applications of Organic Chemistry to Biology and Medicine," New York, 1930. G. B.

ADRENALINE. Synonyms for : Adrenamine, Adnephrin, Epinephrine, Epirenan, Hemisine, Hemostatin, Paranephrin, Renalina, Supracapsulin, Suprarenalin, Supranephrane, Suprarenin.

ADRONOL. *Hexalin*, *Sextol.* Trade names for *cyclo*hexanol.

ADSORBIT. A bleaching earth activated by a preliminary treatment with hydrochloric acid, used in refining petroleum.

ADSORPTION. The terms " adsorption " and " sorption " are applied, in the widest sense, to the concentration of materials in solution or in vapour form at an interface between phases. The adsorption which occurs at liquid—liquid interfaces is of interest in the study of emulsification, and that occurring at liquid—gas interfaces has a bearing on the formation of froths and upon the stability of mists encountered in gas purification processes (*see* ABSORPTION). Adsorption at solid surfaces is most important from an industrial standpoint, either by reason of its relation to processes such as dyeing, extraction, drying, etc., or as a special technique, for example, in decolorisation or solvent recovery. Whilst the special adsorption processes have been developed to a high degree of industrial application, no adequate theory has been advanced which will serve to correlate all known facts.

Vapour Phase Adsorption.—The essential facts of a vapour phase adsorption can be recorded in the form of a curve usually called the adsorption isotherm.

Fig. 1 shows typical data for a carbon adsorbent. In Fig. 2 the values have been plotted logarithmically. Even in the simpler case of vapour phase adsorption, whilst no theory is universally accepted (1), (2), a vivid and useful impression of the essential facts can be obtained by applying the hypothesis of capillary condensation. If the adsorbent be regarded simply as having a microporous structure and it be assumed that the pores are cylindrical, and the surface of the liquid meniscus is a hemisphere, it can be shown mathematically (3) that the vapour pressure p above the meniscus in a capillary of radius r will be less than that at a plane surface p_s, and that the following relationship will be obtained :

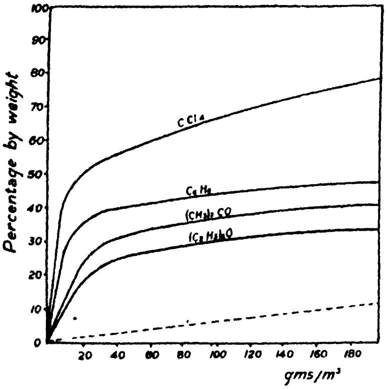


FIG. 1.

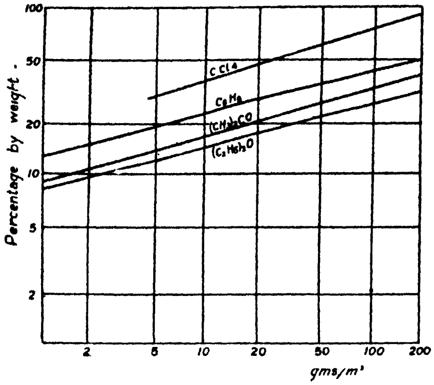


FIG. 2.

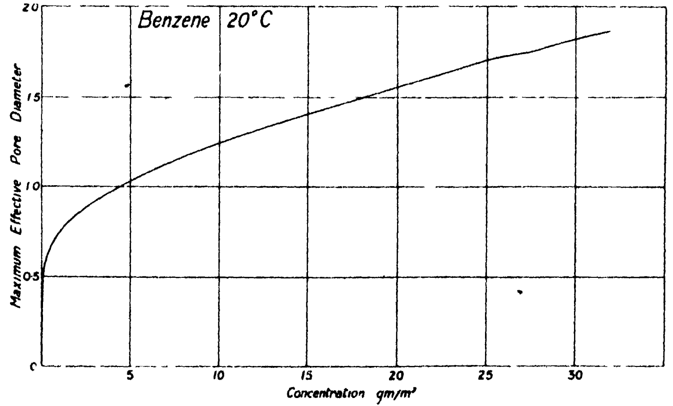


FIG. 3.

$$\text{Log}_e \frac{p}{p_s} = -\frac{2vs}{RTr}$$

where v = molecular volume of condensed liquid, s = surface tension, R = gas constant, T = absolute temperature. By means of this formula (4) it is possible to calculate the maximum size of pore which will be filled with liquid by capillary condensation, under equilibrium conditions, for any given partial pressure or concentration in the vapour phase.

Fig. 3 shows the results of such a calculation for benzene at 20°C. By combining the practical data (4) from adsorption isotherms for different adsorbents, for benzene at 20°C., with the results shown in Fig. 3 a *theoretical* structural analysis of a solid adsorbent may be derived.

Fig. 4 shows the results of such calculations for four different adsorbents. Specially manufactured adsorbent materials are obtainable, the properties of which show that a considerable measure of control over the capillary structure is possible.

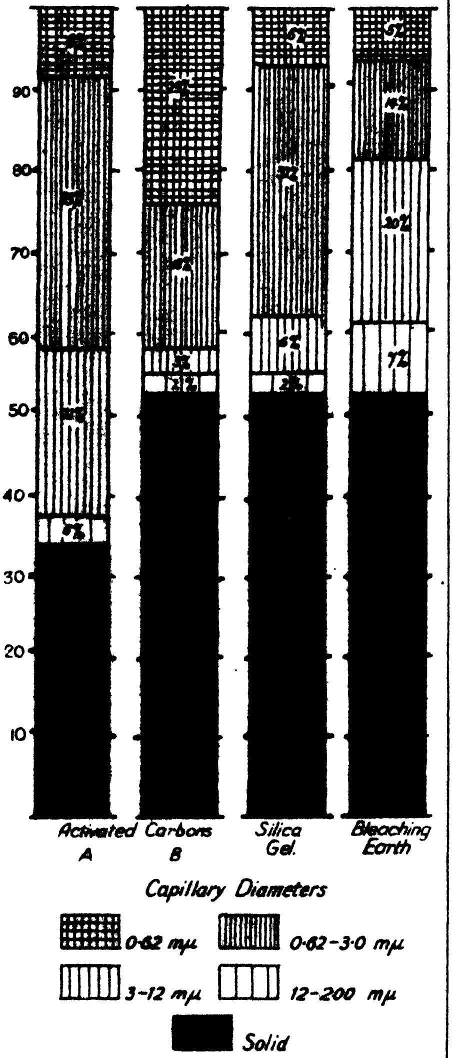


FIG. 4.

The industrial importance of vapour phase adsorption is largely due to the efficiency with which the processes can be worked at very low concentrations, and the quantitative difference between the properties of a solid adsorbent and a liquid absorbent should be noted. In Fig. 1 the dotted line shows the corresponding data for an oil, in equilibrium with various concentrations of benzene at 20°C.

In many processes such as solvent recovery, benzole extraction and air purification, the practical conditions are such that extremely low concentrations are encountered, at which absorption, condensation or compression processes could not be economically applied (4). In a process of recovery of solvents under usual conditions, sufficient suction has to be employed to prevent accidental escape of solvent, with the result that the concentration in the air stream may be reduced to well below 10 gm./cu.m. If inflammable solvents are used it is dangerous to attempt to raise the concentration by reason of the fact that the air-solvent mixture may become explosive. Whilst the fundamental facts have

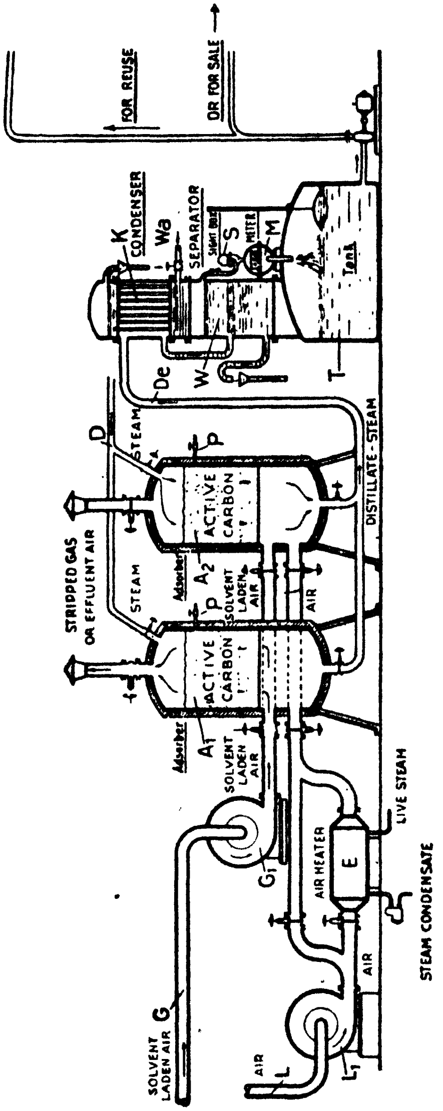


FIG. 5.

been known for years, apart from a limited application to deodorisation, and in gas masks, but little progress was made industrially until after the introduction of the Bayer Process in 1916. The Bayer patent disclosed the method of expelling the solvent by direct steaming into a condenser, this enabling the adsorbed solvents to be recovered and the adsorbents to be regenerated conveniently for further use. This process was subsequently improved and exploited by the Carbo-Norit-Union, and has now been very widely applied in many branches of industry.

A typical arrangement of this system in its simplest form is shown in Fig. 5. The adsorbent carbon is contained in two vessels which are alternately saturated and steamed out. After steaming, warm air may be blown through the adsorbers to dry the carbon. With an installation of this kind it is possible, even at low concentrations, to extract at an insignificant cost over 99% of the solvent contained in the air entering the plant.

This process has been applied extensively to solvent recovery in many industries: *e.g.* manufacture of films, explosives, rayon (cellulose acetate), coated fabrics (4). The adsorption process has also been applied to the extraction of liquid hydrocarbons from gases on a very large scale, *e.g.* recovery of gasoline from natural gas and extraction of benzole from coal gas. This process of benzole extraction is used by the Gas Light and Coke Company at Beckton, East Ham, E.C., where the installation deals with 76,000,000 cu. ft. of gas per day and extracts 22,000 gals. of benzole per day (5). An important feature of the process is that the adsorption removes many impurities from the gas. Fig. 6 shows a Carbo-Union adsorption plant for the recovery of gasoline from natural gas on a large scale. Fig. 7 illustrates the application to the debenzolisation of town gas, the plant shown being capable of dealing with approximately 2,000,000 cu. ft. of gas per day.

The vapour phase adsorption process also finds application in the purification of air and gases. In such cases the general principle of the solvent recovery plant described above may be followed. If, however, the adsorbed substances are of very high molecular weight or rapidly polymerised, it may not be possible to expel them from the adsorbent by steaming. Adsorptive carbon has been employed on a very large scale as a catalyst for the removal of hydrogen sulphide from the water gas used in the manufacture of synthetic ammonia (4).

The adsorption of water is an important factor in the industrial application of adsorbents. As indicated by Fig. 4, it is possible to manufacture qualities of silica gel and activated carbon of similar theoretical capillary structure, and the isotherms obtained on tests with a dry air-benzene mixture may be almost identical. The behaviour of these two substances in contact with water vapour is, however, entirely different, silica gel having very powerful dehydrating properties, taking up as much as 40% by weight of water with a considerable evolution of heat, whereas activated carbon has an unexpectedly low affinity for moisture.

This characteristic property of silica gel has been applied industrially in the drying of large volumes of air, and in the reduction of water vapour pressure in vacuum plants. Since the water can be expelled by heat under suitable conditions, without decomposition or alteration of the gel, the process is more economical than chemical dehydration.

It should be noted that this property of silica gel is a disadvantage in solvent recovery and like processes, since atmospheric air and industrial gases always contain moisture. Whilst silica gel adsorbs moisture in preference to solvents, activated carbon adsorbs solvents in preference to water. The normal moisture content in the air will therefore tend to displace solvent from saturated silica gel (6). If water and benzene are shaken together with silica gel the water is adsorbed, but with carbon the benzene is adsorbed. Whilst this difference does not make the application of silica gel in such processes as solvent recovery impossible, the influence of moisture must be taken into consideration.

Adsorption processes have also been applied to the extraction from gases of hydrocarbons which are gaseous at ordinary temperatures, such as ethylene, propylene, propane and butane. As a general rule the method is applicable for the removal of substances having a critical temperature above usual atmospheric temperatures. Although all adsorbent materials take up permanent gases in considerable quantities, the quantitative relations are not so favourable as in the case of substances which undergo capillary condensation.

At low temperature, however, the behaviour of the permanent gases becomes comparable with that of condensible vapours, and adsorptive materials when cooled by liquid air may therefore be employed to maintain high vacua in closed vessels (7). Whilst carbon is usually employed in work of this kind, other materials have been investigated. Certain zeolites, particularly chabazite, $CaAl_2Si_4O_{12},6H_2O$, after dehydration show excellent results. The phenomena of adsorption at low temperatures and under high vacua have been fully investigated and theories of adsorption have been proposed which are, for scientific work, more satisfactory than the capillary condensation theory, but still not adequate to correlate all observed facts (1), (2), (8). The application of adsorbents in commercial high vacuum technique is of considerable importance, and it is now recognised that some of the difficulties in the production of wireless valves, X-ray tubes, and the like are due to adsorption of gases and vapours by glass and metal parts.

For gas mask purposes, the activated carbons are usually employed, not only because of their efficiency when working at low concentrations, but also by reason of the fact that their indifference to moisture renders them reliable in practice. An adsorbent for gas mask purposes must be capable of adsorbing at extremely low concentrations even when air is passed through at high speed. The conditions to be fulfilled by a gas mask adsorbent are therefore different from those required for a solvent recovery adsorbent.

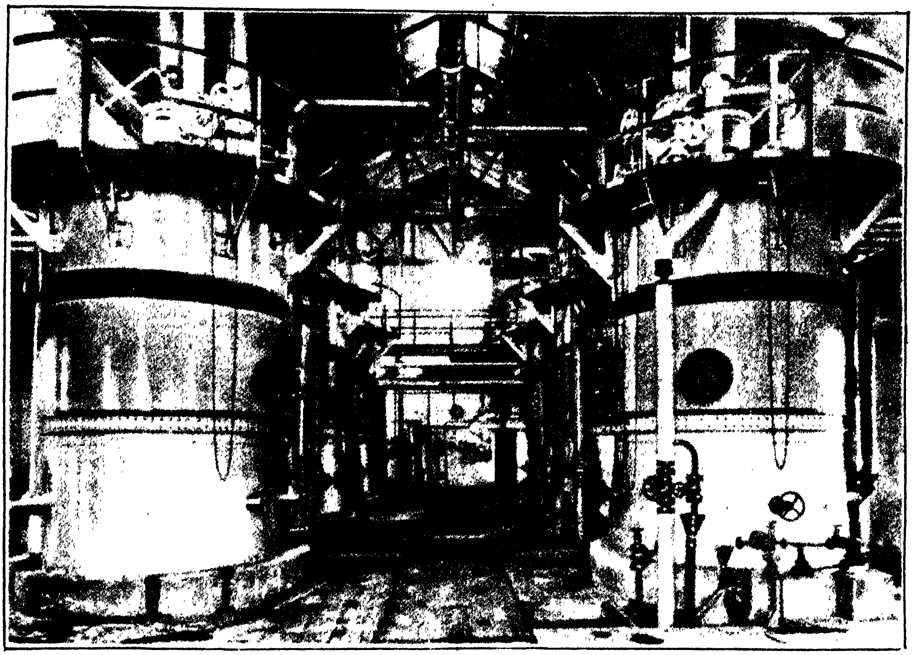


FIG. 6.

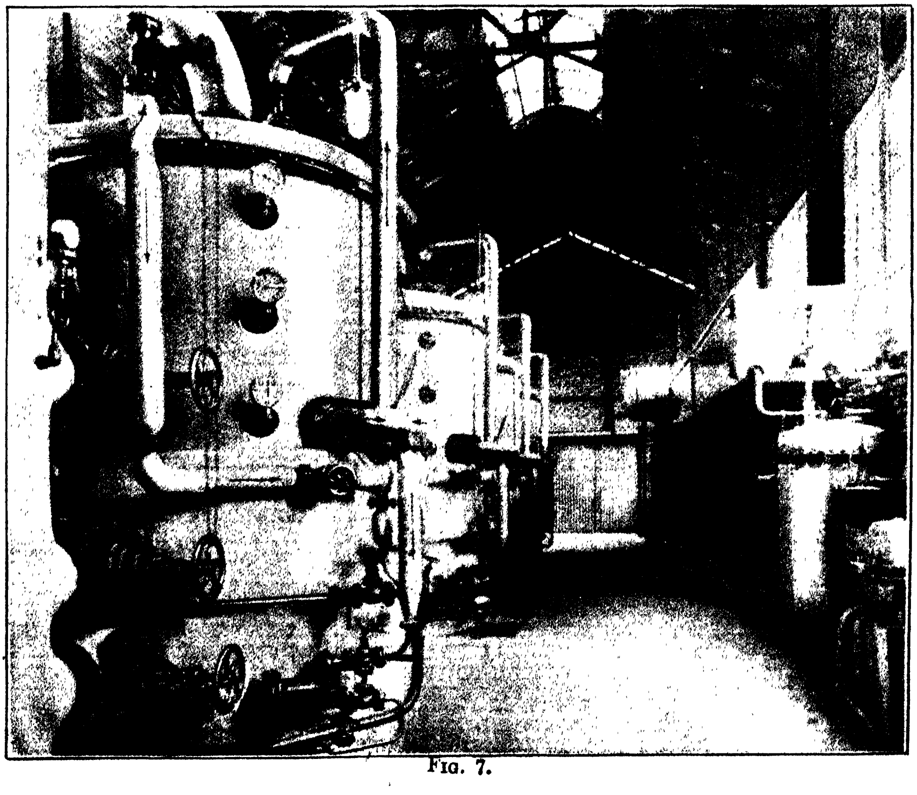


FIG. 7.

In the choice of an adsorbent for a solvent recovery process not only should attention be paid to the adsorption characteristics over the particular range of operating concentrations, but the mechanical properties, such as resistance to abrasion and power to withstand steaming and drying, must be taken into account. It is also important to bear in mind that many commercial solvents contain small proportions of substances of high molecular weight which are not readily steamed out. The type of capillary structure suitable for gas mask adsorbents is therefore not necessarily the best for solvent recovery work.

The testing of adsorbents should always be carried out under conditions of temperature, concentration and humidity which will correspond as closely as possible with the conditions of service. It is quite useless to attempt an extraction by means of air saturated with some such vapour as carbon tetrachloride, *i.e.* at a concentration of over about 800 gm./cu. m., since the practically important concentration may be less than 10 gm./cu. m.

The method of testing should be chosen so as to bring into prominence only the capillaries which will be effective over the practical range of concentrations (14). Tests made with saturated vapour will clearly lead to a value being placed upon capillaries which never come into play.

Fig. 8 shows the adsorption isotherms of two different materials, and it will be clear that whilst material A is more efficient than B at low concentrations, at higher concentrations the positions are reversed.

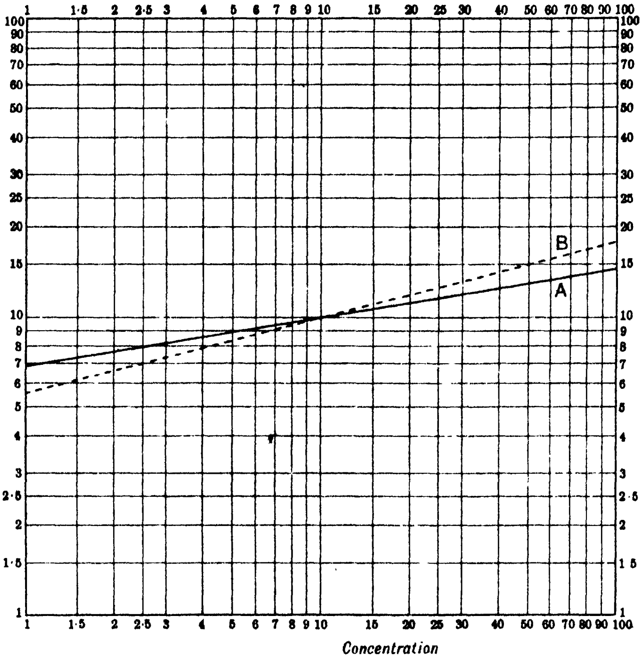


FIG. 8.

Liquid Phase Adsorption.—Adsorption in the liquid phase occurs in almost all industrial processes when a solid is in contact with a solution. Many processes, such as dyeing and lake-formation, are largely adsorptive in character. Occasionally use may be made of the adsorptive properties of precipitated materials in the clarification or decolorisation of solutions, for example, in the purification of water with aluminium salts.

The fundamental facts of liquid phase adsorption are similar to those of vapour phase adsorption. An examination of concentrations under equilibrium conditions will show that a relationship exists resembling the adsorption "isotherm." Fig. 9 shows data for a carbon adsorbent. Whilst the resemblance to vapour phase adsorption is striking, and theoretical analysis has been attempted, unfortunately but little is known about surface tension at liquid—solid interfaces and there is difficulty in deriving a theory of any great practical value. It is clear, however, that the adsorptive power of a solid bears a relation to its surface development or capillary structure.

The most important liquid phase adsorbents are : Bone Charcoal (13), Decolorising Carbons, Bleaching Earths (13) (including clays and bauxite), and Silica Gel (13).

Bone char is extensively used in sugar refining, although within recent years it has been replaced to a considerable extent by decolorising carbons. Bone char contains only about 10% of carbon, and its activity depends almost entirely upon this carbon content which is distributed through its mass in an active form.

Decolorising carbons are specially manufactured and sold under various proprietary names, such as *Norit, Carboraffin, Esbit, Eponit, Darco, Suchar, Sumacarb,* etc. These materials have a much higher activity than bone char, the best qualities, for example, in sugar decolorisation will do the same work as 80 times their weight of bone char. They contain up to 97–98% carbon and can be prepared free from any soluble materials. The very high activity is important in that the dimensions and cost of plant can be reduced.

The adsorptive characteristics of decolorising carbons vary very considerably, and many grades are manufactured to suit the requirements of the different industrial processes in which they are used.

Bleaching earths and clays are chiefly employed in the treatment of oils and other substances where the possibility of contamination with

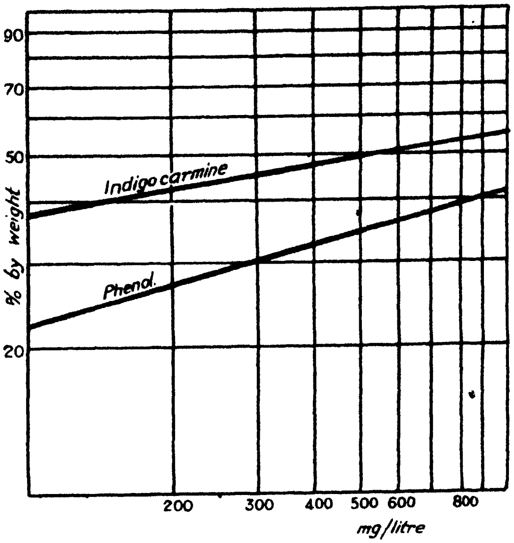


FIG. 9.

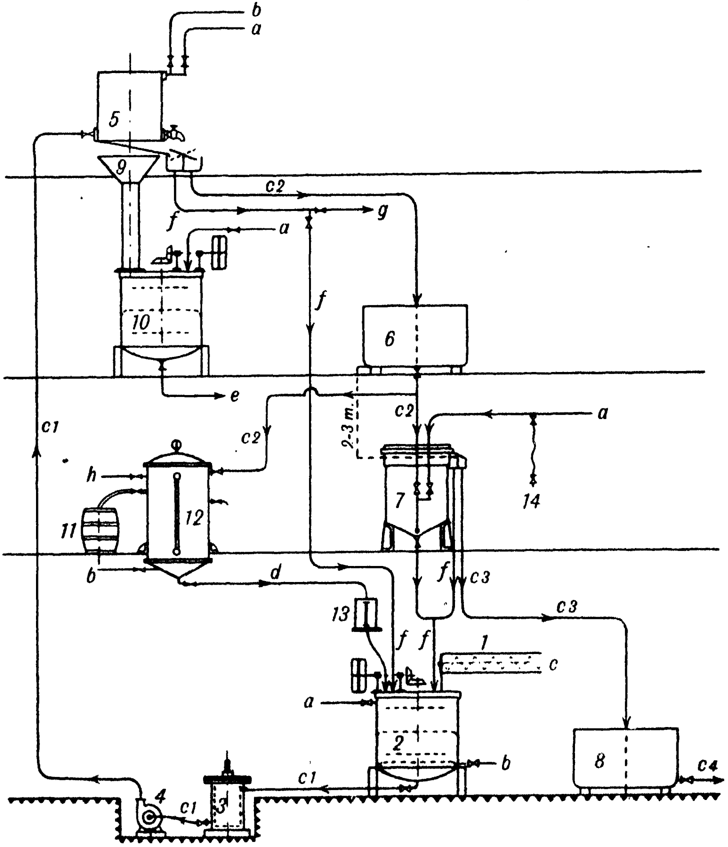


FIG. 10.

soluble inorganic salts does not arise. These adsorbents are sometimes refined by acid leaching of the calcined earths and improved by blending.

In general two types of treatment with liquid phase adsorbents may be applied, *i.e.* a mixing process, in which the adsorbent is stirred up with the solution to be treated and afterwards filtered out ; or a layer-filtration process, in which the raw liquor is passed through a bed of adsorbent. Fig. 10 shows an arrangement for the mixing-in process, and Fig. 11 for a layer filtration system.

The testing of liquid phase adsorbents is also preferably carried out under service conditions whenever possible. In most cases it is desirable not only to test different materials, but to modify the methods of application until the most economical conditions have been ascertained.

When large quantities are used it may be advantageous to regenerate the adsorbents by furnacing to render them suitable for further use. In the case of carbon adsorbents, the regeneration may in certain cases be effected by boiling successively with acid and alkaline solutions.

The adsorption process may also be applied to the purification of water, special qualities of activated carbon being particularly suitable for the removal of tastes and odours and for improving colour. In water purification, a mixing-in process may be used with powdered carbon, or a filtration process may be applied, using granular carbon. In a patented modification powdered carbon may be washed into a sand filter and stirred into the top layer, thus obtaining a reduced consumption of carbon as compared with an ordinary mixing-in system.

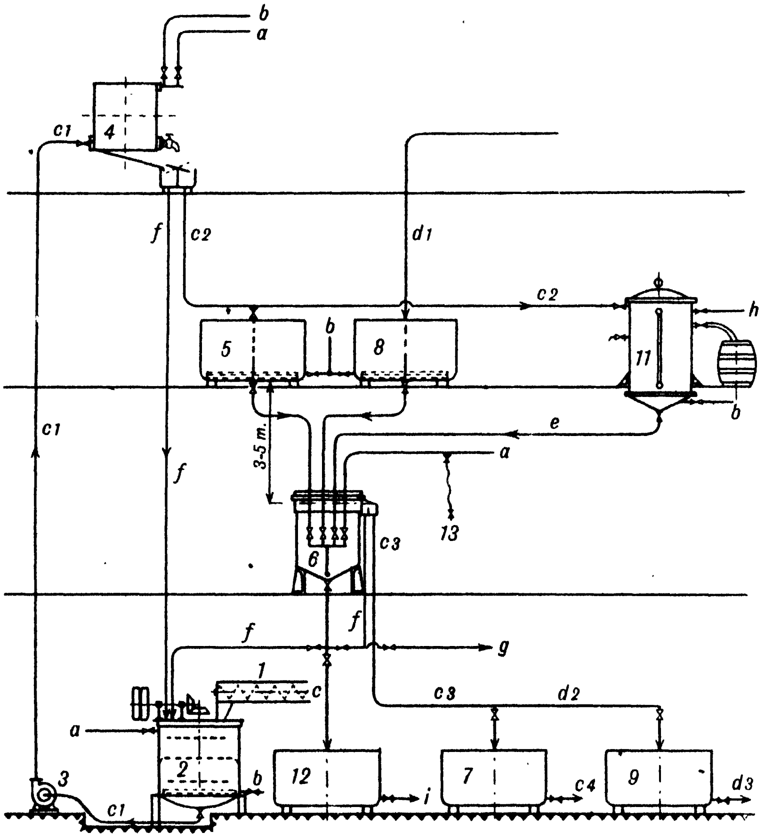


FIG. 11.

Carbon adsorbents are also used for the removal of after-chlorination tastes from water. In this case the removal of chlorinated organic substances is effected by adsorption, but excess of free chlorine is also destroyed by catalytic conversion into sodium chloride. In this process H. Pick (9) has introduced a factor into the design of dechlorination filters of "half value length," *i.e.* the height of column of carbon necessary to reduce the chlorine concentration to one-half, at a velocity of 1 cm./sec., and has demonstrated that halving the depth of the carbon bed requires a reduction in the throughput velocity to one-quarter of the original value.

Further applications of adsorption in water purification are in the removal of traces of oil, benzol, etc., and in the removal of phenols from gas liquor (4).

Manufacture of Adsorbents.—The manufacture of adsorbent materials has been developed into an important industry, and many processes have been patented in connection with the production of activated carbons (*see* Charcoal, Active) and silica gels (10).

Patents have been applied for covering the use of an enormous number of different substances as activators (10). The production of good adsorbent materials requires much experience and strict control in order to ensure that the desired characteristics will be obtained.

In the case of silica gel, the hydrated gel obtained by decomposition of sodium silicate solution with acids under carefully regulated conditions is washed, dried, and heated (11) (12).

Bleaching earths (13) in most cases are derived from naturally occurring materials, *e.g.* bauxite, which are purified by burning or leaching with acids if necessary. They are frequently blended and sometimes improved by addition of activated carbon.

For vapour phase processes and for water filtration it is important that the materials should be obtained in a regular granular form to facilitate the uniform flow of gas, water, and steam.

References.

(1) "The Sorption of Gases by Solid," J. W. McBain, London, 1932 (Routledge).

(2) "The Adsorption of Gases by Solids," S. J. Gregg, London (Methuen).

(3) "Applications of Dynamics to Physics and Chemistry," J. J. Thomson, 1888 (MacMillan); W. Thomson, Phil. Mag. 1871 (4), 42, 448.

(4) Griffiths, J. Inst. Fuel, June, 1935.

(5) Hollings and Hay, J. Soc. Chem. Ind. 1934, **53**, 143.

(6) "Aktive Kohle, und ihre Verwendung in der chemischen Industrie," Bailleul, Herbert, and Reisemann, 1934, Stuttgart (F. Enke).

(7) Dewar, Proc. Royal Soc. 1904, **74**, 122 and 127.

(8) "Hochvakuumtechnik," S. Dushman, 1926, Berlin (Springer).

(9) H. Pick, "Vom Wasser," Bd. V, 1931.

(10) O. Kausch, "Die Aktive Kohle," 1928, Halle (Knapp).

(11) D.R.P. 482176.

(12) O. Kausch, "Das Kieselsaüregel und die Bleicherden," 1927, Berlin.

(13) J. H. Perry, "Chemical Engineers Handbook," 1934 (McGraw-Hill).

(14) Evans, Pearson, and Reisemann, Trans. Inst. Chem. Engineers, 1929, 7.

H. G.

ADSUKI BEAN. Kuroda and Wada (Proc. Imp. Acad. Tokyo, 1934, **10**, 472) isolated from the adsuki bean a purple colouring matter which decomposed at 235°, and yielded phloroglucinol and protocatechuic acid by decomposition with alkali. A tannin-like substance was also isolated, and this, with alkali, gave phloroglucinol and gallic acid.

A. G. P. and E. J. C.

ADUROL. Photographic developer. Adurol-Hauff and Adurol-Schering are the monochloro- (m.p. 103°–104°) and monobromo- (m.p. 110°–111°) derivatives respectively of hydroquinone, $C_6H_3X(OH)_2$.

AEGLE MARMELOS. (Fam. Rutaceæ.) Indian Bæl. Bengal Quince. B. B. L. Dikshit and S. Dutt (J. Indian Chem. Soc. 1930, **7**, 759; A. 1930, 1628) isolated an "active principle" *marmelosin*, m.p. 103°, from the fruit, and from the seeds an oil with the iodine value 126·1. The fresh fruit, which also contains much mucilage, has been used in India as a remedy for dysentery.

AERAL *v.* Alloys, Light.

AERATED AND MINERAL WATERS. The origin of the term "mineral water" is not merely of antiquarian interest, but is still of chemical importance in connection with requirements of the Revenue Authorities. Originally the term was restricted to natural waters containing various salts in solution, and frequently saturated with gases such as carbon dioxide or hydrogen sulphide, and they were regarded as medicinal products. The mineral waters made in imitation of natural products were also at first intended to be used only medicinally, and some were termed "aerated waters" to distinguish them from natural waters saturated with carbon dioxide. The extension of the term "mineral water" to include not only such natural waters as can be used as table beverages, but also artificial aerated beverages such as lemonade and the like, which, strictly speaking, are not mineral waters at all, is a comparatively modern development.

Natural Mineral Waters.—Most natural spring waters have derived their saline constituents from the passage of rain water through deposits of salts, but there is now strong evidence for concluding that certain springs, in particular those at Harrogate, are of magmatic origin (*see* Clarke, 1924, The Data of Geochemistry, U.S. Geol. Survey Bull. 770, p. 213 *et seq.*; Gilligan, Report on the Geological Structures of the Harrogate Area and the Occurrence of the Mineral Waters, 1927; Woodmansey, Analyst, 1936, **61**, 23).

In 1931 the International Society of Medical Hydrology prescribed methods for recording the analytical data and other characteristics of medicinal waters. The classification is standardised according to the chemical, physical or medicinal properties of the waters as follows:—A. *Chemical classification* is based on (*a*) composition in terms of one or more of the most active ions; (*b*) concentration (ionic concentration) in terms of $N/1,000$; (*c*) hydrogen ion concentration in terms of p_H at 20°C. B. *Physical classification* according to (1) Temperature at the source: (*a*) cold, below 20°; (*b*) thermal, 20° to 37°; (*c*) hyperthermal, above 37°C. (2) *Radioactivity*, of (*a*) the water or (*b*) the contained gases. (3) Ionicity expressed in terms *hypotonic*, *isotonic*, *hypertonic*, in comparison with body fluids.

C. *Medicinal classification*, based on analytical data and clinical experience as follows: (*a*) *internal action* (aperient, diuretic, tonic, alterative, etc.), and (*b*) *external action* (temperature effects, sedative, stimulant, etc.). *Disorders* for which the water is indicated are named.

Of the waters classified as "medicinal," those that contain only a small proportion of salts and a large amount of carbon dioxide are used mainly as table beverages. Typical examples of these are Apollinaris water, Selters water, and St. Galmier (French). Other natural waters, such as those of Bath and Malvern, are made more palatable by artificial aeration.

The following table of analyses shows the chief constituents (grouped by the older method) of typical natural mineral waters.

PRINCIPAL SALINE CONSTITUENTS OF MINERAL WATERS—PARTS PER 10,000.

Source	Sodium carbonate	Sodium chloride	Sodium sulphate	Potassium carbonate	Potassium chloride	Potassium sulphate	Magnesium carbonate	Magnesium sulphate	Calcium carbonate	Iron oxide and alumina	Carbon dioxide per litre c.c.	Authority
Apollinaris	12·57	4·66	3·00	trace	—	—	4·42	—	0·59	0·20	—	Bischoff and Mohr
Hunyadi Janos	7·96	13·05	159·15	—	—	0·85	—	160·16	9·33	0·04	—	Knapp
Kissingen	0·04	74·21	2·28	—	0·32	—	2·10	—	7·74	0·24	1026 at 11°C.	Kastner, Bauer, and Struve
Selters .	8·01	22·51	—	—	0·47	0·51	2·60	—	2·43	—	1087 at 15°C.	Struve
Vichy .	48·83	5·34	2·91	3·52	—	—	3·30	—	4·34	trace	508	Bouquet
Wiesbaden	—	68·35	—	—	1·46	—	—	—	4·18	—	200	Fresenius

Artificial Mineral Waters.—Mixtures of salts blended to correspond fairly closely in composition with the saline residues left on evaporating well-known medicinal waters are sold, with directions for preparing solutions which will imitate the respective natural products ; these are frequently aerated. *Seltzer water*, intended to imitate the natural Selters water, is a typical product of this kind, but there is no definite standard for its composition, the proportions of salts being varied to suit the popular demand. It is usually bottled at a pressure of about 120 lb., corresponding with about 45 to 55 lb. in the bottle.

Other artificial medicinal waters include soda water, potash water, and lithia water. Until 1898 these were all official drugs in the British Pharmacopœia, but they are not now included. There is therefore no longer a standard for soda water, and since the old standard of 30 grains per pint is too alkaline to be palatable as a beverage, much of the soda water now sold contains very much less alkali. On the other hand, potash water and lithia water are still used medicinally, and it is therefore reasonable that they should contain a significant proportion of the alkali salt.

Methods of Aerating.—The method of carbonating by compressing carbon dioxide with the aid of a force pump into water contained in a cask became known as the "Geneva process" from the fact that it was first introduced on a manufacturing scale by Paul in Geneva about the year 1790, but in modern mineral water factories the carbonating machinery chiefly employed has been developed from the continuous process invented by Hamilton and perfected by Brahmah. The older cylinder or intermittent "Geneva" process still survives, however, as an auxiliary method in small factories, and is useful when a relatively small amount of liquid, such as lithia water, for which there is only a limited demand, has to be carbonated. The intermittent process is also used for carbonating cider or wines. Its drawbacks are that the pressure diminishes during bottling and that there is considerable loss of gas. The cylinders used in the intermittent process are generally made of copper and are either washed with tin, or preferably lined with block tin. In order to reduce the loss of gas, twin cylinders are sometimes used, one being charged while the other is being drawn down. Fans are provided within the cylinders to agitate the liquid during carbonating and thus obtain more uniform distribution of the gas.

Although the use of carbon dioxide compressed into tubes has largely superseded the direct production of the gas from whiting or sodium bicarbonate, there are yet many places where tubes are not readily obtainable, so that some form of generator must be used. These generators may be horizontal or vertical, and are made of lead or of cast iron lined with lead. Sulphuric acid and a carbonate are introduced in regulated quantities, and the mass is distributed by means of agitators. The carbon dioxide evolved is led into a gasometer, whence it is drawn off into the bottling machine. In the Riley "Safety" generator the agitators work upon a vertical shaft, and an automatic cooler and washer is placed between the generator and soda water pump to cool and wash the gas, thus eliminating the gasometer. When a charge is finished the pipe leading to the pump is automatically closed by means of a plunger. Special devices, including a safety valve, are provided to prevent accidents through the development of too high a pressure within the generator.

After leaving the gasometer or the washer of a Riley machine the gas is pumped, simultaneously with water, into a cylinder or globe, where the water is finely divided and saturated with gas under a pressure indicated upon a gauge. Thence the carbonated water is passed into the bottling machine, and is forced under pressure into the bottles previously charged with a measured quantity of sodium carbonate solution or of filtered lemon syrup, etc. This part of the process is termed "syruping" the bottle, even when, as with soda water, no sugar is present. A "blow-off" valve is used for expelling the air from the bottle before carbonating. This "snifting" process inevitably entails some loss of carbon dioxide and syrup, and has led to the general adoption of automatic bottling machines. The principle upon which these machines is based is that of charging an upper cylinder with the carbonated liquid, and filling the bottles automatically in turn, after creating a counter-pressure. Under these conditions the liquid flows quietly into the bottles, and the soda water will be more perfectly charged with gas than under the old "snifting" system at a higher pressure.

The substitution of liquid carbon dioxide for gas generated from carbonates and sulphuric or hydrochloric acid has led to the designing of many other types of compact bottling machines, in which the gasometer is eliminated. The gas tube is connected with the cylinder by means of a pipe, upon which is an automatic reducing valve to regulate the supply of gas, while water is pumped into the cylinder by means of the pump at the bottom.

In the latest types of machines working on this principle, such as the "Nile" automatic de-aerating and carbonating machine of Messrs. Hayward Tyler & Co., the gas passes in at the bottom of a cylinder through an electrically controlled reducing valve, and the actual gas valve is submerged in the solution tank and has a wide area, to prevent freezing. The flow of the gas is automatically controlled by the pressure within the machine, as indicated upon a gauge. So long as two pointers on the gauge remain apart gas flows into the carbonator, but when they make contact the flow of gas stops. Several gas tubes are arranged in a stand on the machine and are connected with the reducing valve by means of flexible metal pipes, so that one or more may be turned on at the same time.

The water is pumped into the top of the tall cylinder and drops through the gas under pressure, being meanwhile finely sub-divided by a series of saturating plates and glass balls. Any air entering with the water is extracted and driven to the top of the cylinder, whence it escapes. In the larger machines of this type there are three vertical cylinders, thus increasing the rate of carbonation. The smallest machines have an output of 110 doz. 10 oz. bottles per hour, and the largest 1,000 doz. per hour, and they use 20% less gas than the old type of machine.

Tube Gas.—The liquefied gas is prepared from furnace gases which are purified in scrubbers (*see* CARBON DIOXIDE). Another source of liquid carbon dioxide is the gas collected from brewers' fermentation tuns, which is purified and condensed in strong steel cylinders. Sometimes imperfectly purified brewery gas may impart an unpleasant flavour to soda water.

In place of tube gas solid carbon dioxide is frequently used, the holder being connected with an automatic device by which the pressure can be reduced as low as 2 lb.

The pressure at which soda water and mineral water is charged is now usually 50 to 75 lb. to the square inch for bottles and 150 lb. for siphons, a gravity system of filling being frequently used instead of filling at high pressures. These figures are those represented on the pressure gauge of the machine, for the final pressure within the bottle is often very much less. An excess of pressure above a certain limit does not result in the liquid in the bottle containing more gas. The pressure is retained more completely in soda water carbonated in the modern automatic machines than in that bottled by the older system. In the automatic bottling machines working on the counter-pressure system mentioned above, the bottles are brought beneath the filling cylinders on a rotating platform, and each in turn fits tightly into a bell-mouth, the air expelled by the carbon dioxide escaping through a valve, and being ultimately discharged through a valve at the top of the feeding cylinder when a certain pressure is reached. After being filled the bottles are removed by hand and stoppered either by hand or machinery without serious material loss of pressure.

An essential requirement of good bottling is that all air should be expelled from the bottle, as is ensured in the modern machines, otherwise, air being much less soluble than carbon dioxide, the liquid will rush with almost explosive violence from the bottle when opened, but will become flat almost immediately. On the other hand, soda water properly saturated with carbon dioxide and free from air will continue to emit minute bubbles of gas for at least five minutes after leaving the bottle.

Pressure Gauges.—Different methods for measuring the pressure of the gas are in use. In England and the United States of America the zero mark on the dial of the pressure gauge indicates atmospheric pressure, and the succeeding figures represent the number of lb. in *excess* of that pressure. In Germany the dial is graduated in atmospheric pressures in excess of the normal pressure, which is represented by zero; whereas in France, where the same mode of expression is used, the figure 1 represents the normal pressure and the figure 2 corresponds with 1 on the German scale, and with 15 lb. on the British and American scales, and so on.

Sweetened Aerated Drinks. — Lemonade, ginger ale, and similar sweetened "mineral waters" are prepared in the same way as soda water. A concentrated syrup is made from sugar or sugar and water, and this is acidified with citric or tartaric acid and flavoured with an essential oil, which is conveniently added in the form of a "soluble essence."

The syrups are filtered through filter bags into tanks whence they are drawn off into the bottling machine. In this country part of the sugar in the syrup is often replaced by saccharin, but in many of the Dominions the use of saccharin is forbidden. It has the advantage of reducing the cost of the syrup and of acting as a preservative, whilst its drawbacks are its cloying taste, which prevents its being used in more than a certain proportion, and its want of fullness on the palate. To remedy this, glucose syrup is sometimes added to the syrup. Methods of detecting and identifying saccharin are described by Reif, Z. Nahr. Genussm. 1923, **46**, 217 ; Lerrigo and Williams (Ammonia Process), Analyst, 1927, **52**, 337 ; Wagenaar, Pharm. Weekblad, 1932 **69**, 614 ; Analyst, 1932, **57**, 592.

Addition of Saponin.—With the object of meeting the popular demand for a beverage which will retain a frothy head for some time after it has been poured from the bottle, manufacturers frequently introduce a small proportion of "foam heading." This usually consists of an extract of quillaia bark or other preparation of saponin. Such an addition is more necessary for drinks containing saccharin than for all-sugar beverages, which froth more with carbon dioxide. According to the results of experiments by Lohmann (Z. öffentl. Chem. 1903, **9**, 320 ; Analyst, 1903, **28**, 361), saponin has no injurious physiological effects; on the other hand, Bourcet and Chevalier (Pharm. J. 1905, **75**, 691) found neutral saponins of a toxic nature in commercial saponins. The physiological action of saponins was subsequently investigated by Kofler (Chem.-Ztg. 1924, **48**, 702) and by Jacobs (J. Biol. Chem. 1925, **63**, 621). These investigations have shown that the glucosides in saponins are toxic and, in view of this fact, a New South Wales Regulation requires the presence of saponin in mineral waters to be declared on the label.

Methods for the identification and estimation of saponin have been described by Kofler (Z. Nahr. Genussm. 1922, **43**, 278 ; Analyst, 1922, **47**, 403), and Mitchell (Analyst, 1926, **47**, 181) has shown that saponins give a colour reaction with nitrates and sulphuric acid. A method of evaluating saponins as foam producers has been devised by Mond (Chem.-Ztg. 1926, **50**, 85 ; Analyst, 1927, **52**, 42), the hæmolytic index of the foam heading being correlated with a "frothing value."

Fermented Beverages.—Among the products of a mineral water factory are some in which aeration is effected by means of restricted fermentation. Ginger beer is the principal representative of this class. It is made by adding sugar and tartaric or citric acid to a dilute infusion of crushed ginger root, inoculating the liquid with a small quantity of a suitable yeast, and allowing the bottles to stand at the proper temperature until sufficient fermentation has taken place. As a rule the fermented liquid contains less than 1% of absolute alcohol, but occasionally in very hot weather the fermentation will proceed further and the ginger beer may then contain as much as 5 or 6% of alcohol, and be liable to condemnation by the Excise Authorities. The pressure in bottled ginger beer, when ready for consumption, will be about 15 lb. to the sq. in., but with abnormal fermentation it may reach 100 lb. or more and burst the bottle.

Objectionable flavours are sometimes produced by accidental infection of the liquid with wild yeasts, such as may happen in a brewery.

Certain non-alcoholic beverages are prepared by restricted fermentation of an infusion of malt and hops, which is then used as a syrup and bottled with aerated water, as in the preparation of lemonade.

Stoppers of Bottles.—The screw stopper of vulcanite or more rarely, stoneware, with a rubber ring to effect a tight joint which almost completely replaced the ordinary cork for mineral waters, has a serious drawback in that impurities of various kinds may lodge below the rubber and, unless strict cleanliness is observed, may contaminate the contents of the next bottle into which the stopper is inserted. The Crown corking system, which is now widely adopted, has many advantages to recommend it. A cap of tinned steel or aluminium, with a corrugated edge, is pressed down by a machine into a special ridge on the neck of the bottle, while a disc of prepared sterilised cork or compressed cork substitute, covered with parchment paper, which is fitted into the cap, makes an air-tight joint. It is essential that the bottles should be of standard pattern, since otherwise there may be faulty bottling.

Bacteriological Conditions.—It has frequently been claimed that impregnation of a liquid with carbon dioxide effects sterilisation, but in a series of bacteriological examinations of soda water, carried out for the medical officer of the City of London, it was found that not more than 25% of the samples were sterile. In some of the worst specimens the number of micro-organisms was uncountable. As the result of this investigation a meeting of representative mineral water manufacturers was held and it was decided to adopt stringent precautions to guard against bacterial contamination at every stage in the process. These had the immediate effect of raising the standard of purity of soda water throughout the country.

In considering the question of bacteriological purity it is necessary to distinguish between accidental contamination of a particular bottle and faulty manufacture due to want of cleanliness in the factory. If the water supply is pure, efficient inspection of the works at irregular intervals is a better safeguard than the occasional bacterioscopic examination of samples of the mineral waters. After allowance has been made for the various chances of contamination, it is not unreasonable to demand that an average sample of soda water, examined within 24 hours after bottling, should contain not more than 100 organisms per ml. at 20°; nor sufficient *B. coli* to be discoverable in 10 ml. For the standards of bacteriological purity adopted in U.S.A., *see* J. W. Sale (Ind. Eng. Chem. 1930, **22**, 332).

Preservatives in Mineral Waters.—The preservatives most likely to be met with in unsweetened mineral waters are sulphites, solutions of which are frequently used, as in breweries, for cleansing the plant or in washing the bottles.

According to Statutory Rules and Orders, No. 775, of the Ministry of Health, sweetened mineral waters may contain either 70 p.p.m.

of sulphur dioxide or 120 p.p.m. of benzoic acid, and brewed ginger beer may contain 120 p.p.m. of benzoic acid. No declaration is required. Non-alcoholic cordials and fruit juices (sweetened or unsweetened) may contain 350 p.p.m. of sulphur dioxide or 600 p.p.m. of benzoic acid. In these Regulations sulphites are calculated as sulphur dioxide and benzoates as benzoic acid. No other preservative is permissible.

Benzoic Acid.—For the detection and determination of small quantities of benzoic acid, *see* Monier-Williams, Ministry of Health Report No. 39 ; Analyst, 1927, **52**, 572 ; Nicholls (Colorimetric method, after oxidation to salicylic acid), Analyst, 1928, **53**, 19 ; Leather, Analyst, 1931, **56**, 299.

Sulphur Dioxide.—For methods of determining sulphur dioxide, *see* Monier-Williams, Ministry of Health Report No. 43, 1927, Analyst, 1927, **52**, 343, 415 ; Method of Chemists of Manufacturing Confectioners Alliance and of the Food Manufacturers' Federation, Analyst, 1928, **53**, 18 ; Parkes, Analyst, 1926, **51**, 620.

Colouring Matters.—Special solutions of colours (usually aniline dyes) are sold to mineral water manufacturers for colouring syrups used for ginger ale and the like. There is no law against the use of artificial coal tar colours for such purposes, provided they are not one of the following : picric acid, Victoria yellow, Manchester yellow, aurantia, aurine (Ministry of Health, Statutory Rules and Orders, No. 775, 1925).

Fermentations occurring in Mineral Waters.—Apart from excessive alcoholic fermentation in ginger beer, acetic or lactic fermentation may sometimes occur, but this seldom happens when thorough cleanliness is observed. A troublesome form of fermentation, commonly termed " mucoid fermentation " or " viscous fermentation," results in the conversion of the contents of the bottle into a thick, ropy, gelatinous mass. This may be caused by several micro-organisms, such as *B. gelatinosum betæ* or *B. viscosus sacchari*, and is liable to occur when impure sugar is used. When it occurs in an isolated bottle, insufficient cleansing is a chief factor in its production. It has been shown by R. Guyot (J. Pharm. Chim. 1927, **8**, 69) that this objectionable change may be produced by a species of torula which, when the proportion of tartaric acid is low, converts sugars into colloidal dextran.

Metallic Impurities.—Traces of metals are frequently found in aerated waters, and sometimes the contamination is serious. Iron, tin and lead, mainly derived from the action of the liquids upon some part of the plant, are the most common impurities.

Iron is of little importance, apart from the fact that when present in soda water which is added to a light coloured liquid, such as whiskey, containing a trace of tannin, it will produce an objectionable dark colour.

Traces of tin find their way into mineral waters through the action of the acid in syrups upon the tin piping leading to the bottling machines, while lead is derived from solder on the pipes. Such soldering should not be permitted, and flushing of the tin piping with water night and morning effectually prevents material contamination with tin. In some factories glass tubing with rubber connections is used instead of tin piping.

It was shown by Barille (Compt. rend. 1911, **153**, 351) that alloys of lead and antimony are more soluble in Seltzer water than either metal separately.

Another common source of lead in sweetened mineral waters is the citric or tartaric acid, in which it may occur as a manufacturing impurity.

Copper is not often present in more than insignificant traces ; when present, it is usually derived from the action of an acid syrup upon parts of the plant which have been insufficiently tinned.

Arsenic may possibly be derived from glucose used in the preparation of syrups, or from preparations of phosphoric acid, which are sometimes used as a substitute for citric or tartaric acid in the syrups. Some years ago it was asserted that mineral waters could take up traces of antimony from the red rubber rings of screw stoppers (which contain antimony sulphide), but experiments showed that there was no risk of contamination in this way.

For the detection and determination of metallic impurities in mineral waters, *see* Budden and Hardy (Lead, Tin, Copper, Iron), Analyst, 1894, **19**, 169 ; Lander and Whyte (Poisonous Metals), Analyst, 1908, **33**, 450 ; Wichman (Metals in Foods), J.A.O.A.C. 1933, **16**, 321.

Arsenic.—Report of Royal Commission (on Arsenic), Analyst, 1904, **29**, 60 ; Thorpe (Electrolytic Determination), Analyst, 1903, **28**, 349 ; Chapman (Marsh-Berzelius Method), Analyst, 1907, **32**, 247 ; Evans (Reinsch Test), Analyst, 1922, **47**, 1 ; Monier-Williams (Electrolytic Marsh Method), Analyst, 1923, **48**, 112, 262 ; Cox (Iodometric Titration), Analyst, 1925, **50**, 3 ; Cribb (Gutzeit Test), Analyst, 1928, **53**, 152 ; Manley (Gutzeit Test), Analyst, 1929, **54**, 30 ; Report on Arsenic in Food Colouring Materials (Sub-Committee of S.P.A.), Analyst, 1930, **55**, 102.

Copper.—Délépine, Compt. rend. 1908, **146**, 981 ; Callan and Henderson (Sodium diethyldithiocarbonate Method), Analyst, 1929, **54**, 560 ; Haddock and Evers (Copper in presence of Iron), Analyst, 1932, **57**, 495 ; H. Fischer (Diphenylthiocarbazone " Dithizone " Test), Mikrochem. 1930, **8**, 319 ; Lampitt, Hughes, Bilham, and Fuller (Copper in Food), Analyst, 1926, **51**, 327.

Lead.—Tatlock and Thomson (Lead in Citric and Tartaric Acids), Analyst, 1908, **33**, 173 ; Richardson (Lead and Copper), Analyst, 1930, **55**, 323 ; Fairhall (Iodometric Method), J. Ind. Hyg. 1922, **4**, 9 ; J.C.S. Abst. 1922, *ii*, 659 ; Francis, Harvey, and Buchan (Fairhall Process), Analyst, 1929, **54**, 725 ; Allport and Skrimshire, (Diphenylthiocarbazone Extract), Analyst, 1932, **57**, 440 ; Hamence (Colorimetric Methods), Analyst, 1933, **58**, 461 ; Lynch, Slater, and Osler (Determination of Traces), Analyst, 1934, **59**, 785.

Tin.—Buchanan and Schryver, L.G.B. Report No. 7, 1908, Analyst, 1909, **34**, 121 ; Lunde and Mathieson (Determination), J.S.C.I. 1934, **53**, 203.

Zinc.—Von der Heide, Z. anal. Chem. 1925, **66**, 24 ; Fischer, Mikrochem. 1930, **8**, 319.
C. A. M.

AERON. A copper-aluminium alloy, sp.gr. 2·8, resembling wrought iron in its mechanical properties (E. Scheuer, Z. Metallk. 1927, **19**, 16 ; B. 1927, 168.)

AEROSOLS. A term in colloid chemistry for the air dispersoids dust, smoke (solid disperse phase), and fog (liquid disperse phase). The particle size varies from 30μ in dense fogs down to 0·01μ. The coarser particles fall vertically, the smaller exhibit Brownian movement. The light scattered laterally when a fog is traversed by a beam of light is polarised—*Tyndall effect* (Phil. Mag. 1871 (4), **41**, 107, 274, 447). The scattered light is bluish, since the shorter wavelengths are most affected. Gas molecules also scatter light (Rayleigh's theory of the blue of the sky - Raman effect).

Measurements of the concentration, size and electric charge of the particles are important, as these values condition the stability of aerosols (*cf.* V. Kohlschütter, Kolloid-Z. 1927, **42**, 229 ; B. 1927, 687 ; A. Stager, *ibid. idem*, 223 ; B. 823 ; "Smoke" and "Dust," *infra*). F. G. Cottrell (B.P. 5969, 1908) invented the electrical method of dust precipitation in which flue gases are passed between groups of wires or plates maintained at 50,000 to 100,000 volts. Disastrous explosions have been caused by the accidental ignition of the dispersed dust of coal, flour, sugar, cork, aluminium (W. E. Gibbs, "Dust Hazard in Industry," Benn Bros., 1925 ; for coal dust, *see* the publications of the Safety in Mines Research Board, H.M. Stationery Office). It is sometimes practicable to filter out dust. The factors governing its adsorption by filters are discussed by A. Astrom (Svensk Kem. Tidskr. 1929, **41**, 190 ; A. 1929, 1231). Of instruments for measuring the density of smoke may be mentioned those of J. S. Owens (B.P. 372955, 20/5/31 ; B. 1932, 754 ; B.P. 414817, 23/3/33 ; B. 1934, 942). Useful applications of aerosols are seen in the air flotation process of grading pigments and fillers (silica). The extensive literature of aerosols cannot be summarised here ; there are 545 references in "Dust," by S. C. Blacktin, Chapman and Hall, London, 1934; *see also* "Smoke," by R. Whytlaw-Gray and H. S. Patterson, Arnold, London, 1932. The Reports on Atmospheric Pollution of the Department of Scientific and Industrial Research should also be consulted. J. N. G.

ÆRUGO. (Verdigris.) The name given by the Romans to the green rust produced on copper and bronze by exposure to the atmosphere.

ÆSCHYNITE. A rare-earth mineral from Miask in the Ilmen Mountains, southern Urals, described by Berzelius in 1828, and named from αἰσχύνη, shame, in allusion to the fact that at that time no means of separating titanium and columbium was known to chemists. It is a titano-columbate (and thorate) of cerium-metals, calcium and iron, and the composition can be expressed as a combination of a metacolumbate $(Ca,Fe)Cb_2O_6$ with a titanate (and thorate) $Ce_2(Ti,Th)_4O_{11}$. The mineral forms orthorhombic crystals of prismatic habit. It is black or brownish, with a pitchy lustre and conchoidal fracture ; sp.gr. 4·9–5·17, hardness 5–6. The crystals are found with red felspar, biotite and zircon in nepheline-syenite at Miask, Urals. The mineral from Hitterö, Norway, referred to this species by W. C. Brögger in 1879, has since been named blomstrandine (*q.v.*). L. J. S.

ÆSCIGENIN. This sapogenin ester, $C_{35}H_{58}O_7$, m.p. 309°, $[\alpha]_D + 26{\cdot}8°$, is obtained together with glucose and glucuronic acid by partial hydrolysis of *æscin*, $C_{53}H_{88}O_{27}$, the saponin from horse-chestnuts (van der Haar, Rec. trav. chim. 1923, **42**, 1080 ; 1926, **45**, 271). Drastic hydrolysis of æscigenin gives tiglic acid, indicating that it is an ester of the structure $C_{30}H_{51}O_5(O{\cdot}CO{\cdot}C_4H_7)$. That æscigenin is a member of the triterpene group follows from the observation that it gives sapotalin (1 : 2 : 7-trimethylnaphthalene) on selenium dehydrogenation (Ruzicka and van Veen, Z. physiol. Chem. 1929, **184**, 69). F. S. S.

ÆSCULIN, $C_{15}H_{16}O_9$, m.p. 205°, is one of the coumarin glycosides, *e.g.* 6 : 7-dihydroxycoumarin (æsculetin), to which the glucose residue is attached in position 6 (Head and Robertson, J.C.S. 1930, 2434). It is found in horse chestnut bark and leaves : its methyl esters (scopolin and fabiatrin) are likewise known in glycosides. There is a daily periodicity in the content of the leaves where æsculin is mobile (Kerstan, Planta, 1934, **21**, 6767). In the bark of twigs it is not easily translocated and does not function as a carbohydrate reserve. It has been synthesised by Glaser and Kraus (Biochem. Z. 1923, **138**, 183). E. F. A.

ÆTHACOL. *Thanatol.* Catechol monoethylether, $C_6H_4(OH)OEt$, b.p. 210°. Internal antiseptic.

ÆTHOCAINE, synonym for *Abdocain* (*q.v.*).

ÆTHONE. Trade name for ethyl orthoformate, $CH(OEt)_3$, b.p. 146°. Used in bronchial complaints.

ÆTHUSA CYNAPIUM (Linn.). (Fam. Umbelliferæ.) "Fool's parsley" or the "lesser hemlock," a poisonous umbelliferous herb. When dried and extracted with alcohol, yields on distillation a small quantity of an essential oil, and the residue contains a resin, a crystalline hydrocarbon *pentatriacontane*, $C_{35}H_{72}$ (m.p. 74°), and a crystalline alcohol (m.p. 140°–141° : $[\alpha]_D = -35{\cdot}7°$) either isomeric with phytosterol, $C_{26}H_{44}O$, or a lower homologue ; *d-mannitol*, together with a small quantity of a *volatile alkaloid* resembling conine, to which the alleged poisonous character of the herb may be due (Power and Tutin, J.S.C.I. 1905, 938).

AFRAMOMUM AMANIENSE (Fam. Zingiberaceæ). Worsley (Bull. Imp. Inst. 1934, **32**, 195 ; B. 1934, 988) describes the essential oils from leaf, peel, and seeds respectively, as follows : ester values 7·5, 4·3, 100·9 (after acetylation 31·9, —, 241·1) ; d^{20} 0·8935, 0·892, 0·8971 ; n_D^{20} 1·4879, 1·4835, 1·4743. The oils contain the hydrocarbons α- and *β-kayene*, $C_{16}H_{28}$, b.p./8 mm. α- 33·5°–34·5°, β- 44·5°–45·5°. The seed oil contains *geraniol* 47·0% and *geranyl acetate* 35·3%. For another report on the seed oil, *cf.* Anon (Bull. Imp. Inst. 1934, **32**, 195 ; B. 1934, 987).

AFRAMOMUM MALA K. Schun., Worsley (Bull. Imp. Inst. 1934, 32, 253 ; B. 1934, 988). Leaf, peel and seed oils respectively, ester values 10·5, 6·0, 3·4 (after acetylation 35·6, 54·2, 31·1). Hydrocarbons 77·0, —, 67·0%. α- and *β-Kayene* 50·0, 73·0, 37·3%. Caryophyllene 24·6, 4·0, 4·1% ; cineole —, —, 41·4%.

AFRAMOMUM MELEGUETA (Fam. Zingiberaceæ). Grains of Paradise. Guinea Grains. The seeds, formerly used as a spice, contain a pungent essential oil and *paradol*, $C_{20}H_{28}O$ (?) (Gildemeister, Aetherische Oele, 1929, ii, 450). Used in veterinary medicine.

AFRICAN FIBRE. *Crin végétal.* Vegetable curled hair. The leaves of the North African fan palm, *Chamærops humilis*, when disintegrated under a jet of water yield fibres which are used in upholstery as a substitute for horsehair.

AFRICAN MARIGOLD. *Quercetagetin* was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier de la Source (Bull. Soc. chim. 1877 (ii), 28, 337), who state that it also occurs in other varieties of the same plant. Perkin (Chem. Soc. Proc. 1902, 18, 75 ; J.C.S. 1913, 103, 209) studied the subject in greater detail and isolated the colouring matter, which is largely present in the flowers as glucoside, by diluting a concentrated alcoholic extract with water which precipitated a viscous impurity, and this was removed with ether. The clear liquid, treated when boiling with addition of a little hydrochloric acid, deposited after cooling only a small bulk of the colouring matter, and repeated extraction of the solution with ether was necessary for its economical isolation. The crude product thus obtained could be crystallised from dilute alcohol, but for complete purification it was necessary to prepare the acetyl derivative, and after recrystallisation to hydrolyse this in the usual manner.

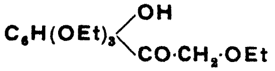
Quercetagetin, $C_{15}H_{10}O_8$, or as crystallised from dilute alcohol $C_{15}H_{10}O_8,2H_2O$, forms pale yellow glistening needles or leaflets resembling quercetin in appearance and melts at about 318°. Very dilute alkali dissolves it with a pure yellow colour which by air oxidation becomes olive and finally deep brown, but these changes are not so marked when a stronger alkali (10%) is employed. Alcoholic ferric chloride produces an olive-green coloration, whereas cold alcoholic lead acetate forms an orange-red precipitate which, on keeping, becomes yellower and finally develops a green tint. On fusion with alkali protocatechuic acid is obtained together with a phenolic product which, however, quickly oxidises and has not yet been identified.

Quercetagetin readily yields oxonium salts with mineral acids, *e.g.* with sulphuric acid fine orange needles of the sulphate,

$$C_{15}H_{10}O_8,H_2SO_4,$$

are obtained. The following are described : *monopotassium quercetagetin*, $C_{15}H_9O_8K$; *hexaacetylquercetagetin*, colourless needles, m.p. 209°–211° ; *quercetagetin pentamethyl ether*, pale yellow needles, m.p. 161°–162° (*monoacetyl* derivative, m.p. 161°–163°) ; and *quercetagetin hexamethyl ether*, colourless needles, m.p. 157°–158°.

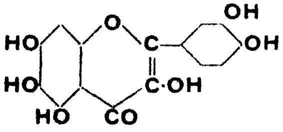
Quercetagetin hexaethyl ether, $C_{15}H_4O_2(OEt)_6$, m.p. 139°–141°, yields oxonium salts analogous to those of quercetin pentamethyl ether, and when hydrolysed with alcoholic potassium hydroxide gives protocatechuic acid diethyl ether, and *quercetagetol tetraethyl ether*, prismatic needles, m.p. 46°–48°, to which the constitution



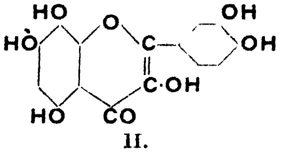
$$C_6H(OEt)_3\left\langle\begin{matrix}OH\\CO{\cdot}CH_2{\cdot}OEt\end{matrix}\right.$$

is assigned. The latter yields the *oxime* $C_{15}H_{25}O_6N$, m.p. 93°–95°, and when oxidised with alkaline permanganate *quercetagetinic acid*, m.p. 100°–102°, is produced.

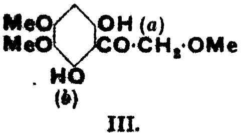
Perkin concluded therefore that quercetagetin is a pentahydroxyflavonol isomeric with gossypetin, the colouring matter of *Gossypium herbaceum*, each apparently containing a tetrahydroxybenzene nucleus, and he commented on the probability that these flavonols are hydroxyquercetins (I and II). A synthesis of a hydroxyquercetin described by Nierenstein (J.C.S. 1917, 111, 4) threw some doubt on the correctness of this view in the case of one at least of the two colouring matters, but the results of Baker, Nodzu, and Robinson (J.C.S. 1929, 74) confirm the work of Perkin in all details. These authors show that both quercetagetin and gossypetin are derivatives of 1 : 3 : 4 : 5-tetrahydroxybenzene, and possess respectively the constitutions I and II. The synthesis (B.N. and R.) of quercetagetin was effected as follows : 4 : 5-dimethoxyresorcinol and methoxyacetonitrile yield, by the Hoesch reaction, the trimethoxyresacetophenone (III). That this substance has formula III and not IV was deduced from the fact that the flavone (V), obtained by veratroylation, gave indications of a free hydroxyl group in the 5- and not the 7-position. The properties of the product were identical with those of the



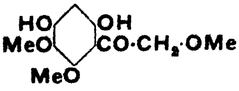
I.



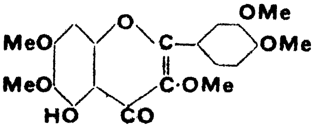
II.



III.



IV.



V.

pentamethyl ether obtained by Perkin by methylation of quercetagetin, and it is well known that the hydroxyl in position 5 offers the greatest resistance to methylating agents. From 5-hydroxy-3 : 6 : 7 : 3′ : 4′-pentamethoxyflavone (V) quercetagetin was obtained by demethylation. The formation of the pyrone ring during veratroylation of III might take place in the direction (*a*) or (*b*) in the formula ; hydroxyl (*a*) is evidently involved, otherwise the flavonol obtained by demethylation would be gossypetin (II), the structure of which has been confirmed by synthesis (*cf.* COTTON FLOWERS).

Quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters. Dull olive-yellow, yellow-orange, brown and brownish-black shades are obtained on chromium, aluminium, tin and iron mordants respectively.

A trace of a more sparingly soluble colouring matter is present in the flowers and represents about 1% of the crude quercetagetin referred to above. It crystallises from alcohol in somewhat indefinite groups of minute needles and dissolves in alkaline solutions with an orange colour passing to green on dilution with water. Though similar in appearance to rhamnetin (quercetin monomethyl ether) it does not contain a methoxyl group.

Dyeing properties of the flowers.—Employing mordanted woollen cloth, the following shades are produced : yellowish-brown (chromium), pale dull yellow (aluminium), deep yellow-orange (tin), and brownish black (iron). As quercetagetin mainly occurs in the flowers as glucoside, their tinctorial effect is evidently due to this latter. A. G. P. and E. J. C.

AFRIDOL. *Mercuretol.* Sodium 3-hydroxy-mercury-*o*-toluate,

$$C_6H_3(CH_3)(COONa)HgOH.$$

Antiseptic, and has been recommended for skin diseases.

AFWILLITE, hydrous calcium silicate, $3CaO{\cdot}2SiO_2{\cdot}3H_2O$ or $2H_2CaSiO_4{\cdot}Ca(OH)_2$, since part of the lime is readily extracted by water. The colourless monoclinic crystals form bundles of prisms up to 11 cm. long. It was found by A. F. Williams, after whom it is named, in the Dutoitspan diamond mine at Kimberley, South Africa, where it occurs as a secondary mineral in a dolerite intrusion in the diamond-bearing kimberlite (J. Parry and F. E. Wright, Min. Mag. 1925, **20**, 277). Later it was found as minute crystals in the metamorphosed contact-rock at Scawt Hill, Larne, Co. Antrim, where dolerite has intruded chalk. Here it occurs with spurrite ($2Ca_2SiO_4{\cdot}CaCO_3$) of which it is a derivative (C. E. Tilley, Geol. Mag. 1930, **67**, 168). L. J. S.

AGALITE. A name used in the paper-making trade for a fibrous variety of the mineral talc, a hydrated magnesium silicate,

$$H_2Mg_3Si_4O_{12}.$$

It is white with a tinge of green, and is readily reduced to short, fine fibres. It is obtained almost exclusively from the district near Gouverneur, in St. Lawrence Co., New York, about 70,000 tons, valued at $10 per ton, being produced annually, and practically all of it is used in the American paper trade. It gives weight and body, and produces a fine gloss on the surface of the paper. L. J. S.

AGALMATOLITE, or Pagodite. A soft stone much used in the East, especially in China, for carving small statues and figures, as signified by these names. At least three mineral species appear to be included under these terms, viz. pyrophyllite, steatite and pinite ; but it is to the compact forms of the first of these that they are perhaps more generally applied. In addition to their compact nature and low degree of hardness, they have in common a greasy or soapy feel : in colour they are white, greyish, greenish, yellowish, etc., often with mottling. Pyrophyllite is a hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$; steatite, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$; and pinite is an alteration-product consisting largely of a finely scaly muscovite-mica, a hydrated potassium aluminium silicate, $H_2KAl_2Si_3O_{12}$. Besides being employed as material for carving, these minerals are used for slate-pencils (*pencil-stone*) and for tailor's chalk (*French chalk*).

Extensive beds of compact pyrophyllite are quarried in the Deep River region in North Carolina, the material being mainly used for making slate-pencils. At Fukuye, in Goto Island, in the south of Japan, a compact mineral allied to pyrophyllite is mined under the name of "rōseki" (meaning "greasy stone" in Japanese) ; it is crushed, washed, and prepared very much like china-clay, and the product used for making fire-bricks and, to a smaller extent, in the manufacture of porcelain and paper. This material contains SiO_2 53–58%, Al_2O_3 32–36%, H_2O 7–9%. L. J. S.

AGAR-AGAR. Bengal or Japanese isinglass. The seaweed from which the agar is obtained on drying, generally the red algæ of the *Gelidium* species, grows in profusion in the Orient. It is marketed either as small transparent strips or as a powder and is of great importance owing to its colloidal properties. It is employed as a size substitute (the gelatinising power is claimed to be greater than that of gelatin) and it is also of great assistance in the electroplating of lead. It is used as a laxative and in the United States of America is employed in the manufacture of cheap ice-cream as its jelly does not liquefy as readily as that of gelatin. In China agar-agar is used as an ingredient of "bird's nest soup." It is widely used in colloid chemistry for the preparation of sols and gels and a solution of 1 part in 500 parts of water is still gelatinous in the cold ; 20 grms. of agar-agar are, however, liquefied in the cold by a solution of 150 grms. of hydrated calcium nitrate in 130 grms. of water. Pure agar-agar is also extensively used as a culture medium in bacteriology, for example, in the culture of paratyphoid germs. Injected intravenously into guinea-pigs it may produce a typical analphylactic shock and death ; it also inhibits the bacteriophage reaction.

Agar (the Malayan plural is formed by repeating the singular) can readily be differentiated from gelatin by the fact that it gives a violet colour with the dyestuff thionine blue, whereas gelatin develops a blue shade ; and it can be differentiated from starch as it does not give the characteristic blue colour with iodine, *cf.* AGAR, REACTIONS OF.

The presence of sulphur in agar is indicated by the production of hydrogen sulphide during the growth of certain bacteria on agar. Neuberg and Ohle (Biochem. Z. 1921, **125**, 311) and Samec and Ssajevič[1] (Compt. rend. 1921, **173**, 1474) concluded that agar is essentially a sulphuric ester of gelose, the latter authors adducing the formula $(C_6H_{10}O_5)_{57},H_2SO_4$. Fairbrother and Mastin (J.C.S. 1923, **123**, 1412) consider that it consists principally of the calcium salt of an acid sulphuric ester $(ROSO_3)_2Ca$ (*see also* Lüdtke, Biochem. Z. 1929, **212**, 419). Takahashi and Shirahama (Amer. Chem. Abstr. 1934, **28**, 5412) obtained from hydrolysed agar a gelatinous substance, *hydrato-kanten-δ*, a white, tasteless amorphous powder of indefinite melting-point, insoluble in ethyl alcohol and ether, yielding mucic acid on oxidation. From the hydrolysis mother liquors, after the removal of the above product, *hydrato-kanten-γ* was precipitated by ethyl alcohol; this appears to be an ethereal sulphate of the type $R'(SO_4)_nCa$.

Knowledge of the physico-chemical properties of agar-agar is due to Fairbrother and Mastin (*l.c.*), who found that "heating a 2% solution, 0·01 *N* with respect to hydrochloric acid for 30 minutes destroys the gelling power" and that agar-agar behaves quite differently from gelatine as regards its swelling in acids and alkalis. These authors state that "the free acid swells less in water than the calcium salt and its swelling is still further diminished by the presence of an acid, when the decrease is nearly proportional to the p_H of the solution. The effect of hydrochloric, sulphuric, oxalic, acetic and phosphoric acids is almost the same at the same p_H. Agar-agar swells more in very dilute caustic soda solutions than in water; in more concentrated alkalis the swelling is less than it is in water. These results support the view that the swelling is governed by the chemical reaction between the medium and the sulphuric ester. The behaviour of agar-agar as an electro-endosmotic diaphragm further supports the theory that the framework of an agar gel consists of hydrated undissolved sulphuric esters and the electronegative sulphuric ester complex."

The use of agar-agar in colloid work requires preparations of a high standard of purity and convenient methods of purification are given by Herzfeld and Klinger (Biochem. Z. 1920, **107**, 268) and Iwase (J. Tokyo Chem. Soc. 1920, **41**, 468). An analysis of such a purified sample shows : moisture content 21·36%, ash content 3·75%, d^{21} 0·7190, p_H 4·05 (hot 1% solution), and heat of combustion 4,870 calories. Harvey (Amer. J. Pharm. 1925, **97**, 66) states that the ash content can be reduced from 3·75 to 0·81% by electrodialysis. I. M. H. and R. F. P.

AGAR, REACTIONS OF. On hydrolysis with 5% sulphuric acid solution, agar yields galactose which reduces Fehling's solution, thus distinguishing it from gelatin and isinglass, both of which are also differentiated from agar by the fact that they yield ammonia when heated with soda lime.

A cold solution of agar (like gelatin) gives a precipitate with tannic acid.

When 0·5 c.c. *N*/10 iodine solution is added to 10 c.c. of a boiling 0·02% agar solution which is then rapidly cooled a dark purple colour is produced, a brownish colour only if added to a similar cold solution.

Detection in jams and jellies.—The ash after treatment with hydrochloric acid or, preferably, the residue obtained by centrifuging a 5% aqueous solution is examined microscopically for diatoms, especially the disc-shaped *Arachnoidiscus Ehrenbergii*, and for sponge spicules (B.P.C. 1934, 74).

AGAROBILLA *v.* ALGAROBILLA.

AGATE. A native form of silica consisting mainly of chalcedony (*q.v.*) and showing a more or less concentric arrangement of differently coloured layers or bands. The layers differ not only in colour but also in translucency, porosity and crystalline structure. Some layers show the minutely fibrous structure of typical chalcedony, others are more dense and cryptocrystalline, while some may consist of crystalline quartz, or again of opaline silica. Some of the layers containing larger amounts of impurities and colouring matter may be more of the character of jasper, as in the agate-jaspers or jasp-agates. The material has been deposited layer upon layer from solution in a colloidal form and subsequently solidified in a partly crystallised condition. The deposition has taken place as a lining in rock cavities, proceeding inwards from the margins of the cavity. In the majority of cases the containing rock is a volcanic rock of basic composition (*i.e.* containing no free primary quartz), the commonest home of the agate being the steam cavities of basaltic rocks. The movement of the molten lava has caused the steam cavities, originally spherical, to be drawn out into almond shapes in the direction of the flow. These almond-shaped, or amygdaloidal, cavities may subsequently become filled with secondary mineral matter of various kinds, derived from the primary minerals of the rock by the action of the hot vapours and solutions which are always present in igneous magmas. Such secondary minerals—calcite and various zeolites – which are commonly associated with agates, have probably been formed while the rock was still hot. The exact conditions of deposition and mode of formation of agates have, however, given rise to much discussion. With the weathering of such an amygdaloidal rock the agate-amygdales, being more resistant, are set free, and may be easily separated from the clayey matrix, or they are washed away and broken up in streams and rivers.

The artificial deposition of gelatinous silica in forms closely resembling those of certain agates has been effected by J. I'Anson and E. A. Pankhurst (Min. Mag. 1882, **5**, 34). A strong acid is introduced by means of a pipette into a solution of an alkaline silicate containing a certain proportion of alkaline carbonate ; the bubbles of carbon dioxide set free become coated as they ascend with gelatinous silica. Agate-like structures have also been produced by Liesegang by the diffusion of one saline solution into another in a gelatinous medium (R. E. Liesegang, "Geologische Diffusionen," Dresden and Leipzig, 1913; "Die Achate," Dresden and Leipzig, 1916; Achat-Theorien, Chem. Erde, 1931, **6**, 143).

---

[1] The name is Isajevič in the complete account of the work (Koll. Chem. Beihefte, 1922, **16**, 285).

Many trivial varieties of agate are distinguished, depending on the patterns presented by the several layers of the stone. For example, fortification-agate, eye-agate, ring-agate, riband-agate, brecciated-agate, etc. *Onyx* is an important variety, differing simply in that the layers are plane, thus enabling cameos to be engraved in relief in one layer with a background in another differently-coloured layer. A typical onyx with alternately white and black layers is however, of rare occurrence in nature, and has usually been produced by artificial colouring, as explained below. In carnelian-onyx the layers are red and white, and in sardonyx brown and white. Moss-agates, mocha-stones, dendrites, etc., are chalcedonies with enclosures of various kinds.

The artificial colouring of banded chalcedony, or the intensification of the coloration of agates, for the production of ornamental objects was probably known to the ancient Romans, and was practised by the Italian cameo-workers of the Middle Ages. The art was for a time lost, and again came into use at Idar in Germany about the year 1820, where it has been much developed and extensively used. Indeed, practically all the fashioned and polished stones now placed on the market have been artificially treated.

A *black* colour is obtained by soaking the well-dried stones for some weeks in a warm dilute solution of sugar or honey, or in olive-oil, and, after washing, immersing them in warm sulphuric acid. The organic matter absorbed by the more porous layers of the stone is thus carbonised. In case the black coloration is too intense it may be softened by the action of nitric acid. A rich *brown* colour has recently been produced in some translucent stones, giving them somewhat the appearance of garnet, by soaking them in brown sugar-candy and then igniting. A *red* colour is produced by saturating the stone with a solution of an iron salt and igniting. A *yellow* tint inclining to lemon-yellow is imparted by digesting the stones in warm hydrochloric acid. *Blue*, ranging from the deepest indigo to delicate sky-blue, is produced by soaking the stones first in a solution of ferrous sulphate and afterwards in a solution of potassium ferrocyanide. Such a colour and also lemon-yellow are, however, unknown amongst naturally coloured agates. The blue-coloured stones have often been passed off as lapis-lazuli, but they are readily distinguished from this by their greater degree of translucency and hardness, and the absence of specks of iron-pyrites. *Green* colours, resembling that of the natural chrysoprase, have been produced by the use of salts of chromium and nickel. Finally, various fancy and quite unnatural colours have been produced by simply dyeing the stones with aniline dyes; these colours fade on exposure to light, and finally disappear. On the history of colouring agates, *see* Nöggerath, Die Kunst, Onyxe . . . zu färben, Karsten's Archiv, 1848, **22**, 262; and on the methods now in use at Idar, O. Dreher, "Das Färben des Achats," Idar, 1913.

The agate-cutting industry has long been centred at Idar and Oberstein on the Nahe, a tributary of the Rhine, and originally the stones were obtained locally from the amygdaloidal melaphyre of the Galgenberg. But since 1827 enormous quantities have been imported from Uruguay and the neighbouring Brazilian state of Rio Grande do Sul. In India, agates and other varieties of chalcedony are abundant in the trap rocks of the Deccan plateau, and have long been worked by the native lapidaries. The well-known "Scotch pebbles" are prettily coloured agates from Forfarshire, Perthshire, etc. Many localities in America and Australia might also be cited.

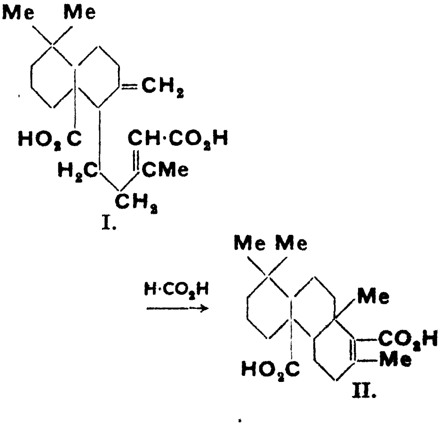
Besides being used for a great variety of small ornamental objects, agate finds technical applications in the construction of pestles and mortars, burnishers for gold-workers and bookbinders, smooth stones for paper and card manufacturers, rollers for ribbon makers, and pivot supports for balances, magnetic needles, etc. It may be remarked, however, that an "agate mortar" need not necessarily show the coloured banding of a true agate, but may just as well be cut from an unbanded chalcedony.

On the agate industry, *see* G. Lange, "Die Halbedelsteine . . . und die Geschichte der Achatindustrie" (Kreuznach, 1868); Upmann, Beit. z. Gesch. d. Graftsch. Oberstein (Mainz, 1872). On Scottish agates, *see* Guide to the Collection of Scottish Agates, Royal Scottish Museum (Edinburgh, 1899); M. F. Heddle, "The Mineralogy of Scotland" (Edinburgh, 1901). On agate in general, *see* M. Bauer, "Edelsteinkunde," 3rd edit. (Leipzig, 1928–32), and Engl. transl., "Precious Stones," by L. J. Spencer (London, 1904); R. Brauns, transl. by L. J. Spencer, "The Mineral Kingdom" (Esslingen, 1912); O. C. Farrington and B. Laufer, "Agate," Field Museum, Chicago, Geol. Leaflet No. 8, 1927; H. Heinz, Chem. Erde, 1930, **4**, 501. L. J. S.

AGATHIC ACID. Agathic acid (I),

$$C_{20}H_{30}O_4,$$

m.p. 203°–204°, $[\alpha]_D$ +56°, is obtained from Manila and kauri copals (Ruzicka and Hosking, Annalen, 1929, **469**, 147).



I.

II.

It is isomerised by formic acid to the tricyclic monoethenoid iso*agathic acid* (II), m.p. 287°–288°, $[\alpha]_D$ +12·8° (Ruzicka and Hosking, Helv. Chim. Acta, 1930, **13**, 1402 ; 1931, **14**, 203).

F. S. S.

AGATHIN. Trade name for salicyl-*α*-methylphenyl hydrazide,

$$HO{\cdot}C_6H_4{\cdot}CH : N{\cdot}NMePh,$$

formerly used as a remedy for neuralgia and rheumatism.

AGAVE. (Fam. Amaryllideæ.) *Sisal.* Species of large plants with succulent leaves grown in tropical America and E. Africa, provide fibres of great importance for twine and ropes, especially sisal hemp from *A. rigida.* False sisal from *A. decipiens* is finer and lacking in strength. Tampico hemp or Mexican fibre comes from *A. heteracantha.* The fibre is simply prepared by scraping mechanically the pulp from the leaves in a current of water. For cordage, genuine sisal is only surpassed by Manila hemp, but it is less flexible and does not resist sea water. It is sometimes known by the Yucatan name "henequen." *A. amaniensis* (Tanganyika) fibres are in some respects superior to No. 1 African sisal (Bull. Imp. Inst. 1934, **32**, 540). Pulque, the beverage of the Mexican natives, is prepared by natural fermentation of the juice of *A.* species (*e.g. A. americana*) which contain the inactive reducing sugar *agavose*, $C_{12}H_{22}O_{11}$. Because of their saponin content the leaves are used locally instead of soap.

Literature.—Matthews, "Textile Fibres," 1924 ; Encyc. Brit., 14th ed. **18**, 762 ; **9**, 214 ; **19**, 545 ; **20**, 720 ; **22**, 494 ; and Bull. Imp. Institute, cited ; U.S.D., 21st ed. 1187, 1188.

J. N. G.

AGEING. ACCELERATED AGEING OR WEATHERING.

Accelerated Methods for Determining Performance Value of Protective Coatings.—The term "protective coating" in the main is intended to include paints, varnishes and lacquers as applied to wood, iron and steel, plaster, concrete and similar surfaces, these considerations will apply also to the examination of bituminous felting, artificial leathers, oil-cloths, and related products and indeed to anything such as, for example, leather, to which paint or other organic material may be applied for protection or decoration. In any event the durability and performance value of "paint" films, using this description in the widest sense as indicated above, must be considered in relation to the background and support as well as in relation to the disturbing or weathering influences.

It is, of course, common practice to carry out exposure tests on all classes of materials under such conditions as the material is expected to meet in ordinary normal use, but tests of that character necessarily occupy the whole normal life of the material ; the accumulation of data on that basis is costly and slow. In so far as such tests are conducted to produce maximum effect (if that be possible) they may be considered as accelerated tests. For example, it is quite usual to expose painted panels or other specimens to the atmosphere in an exposed location such as a high roof in a position likely to receive maximum sunlight, by setting them facing South at 45° to the horizontal. It is obvious that in temperate northern latitudes such panels will receive more sunlight per unit area than if they were placed in a horizontal or vertical position. This kind of exposure is usually described as "natural," but as so little of the paint under test, even if applied to a house, would be likely to be exposed in that precise manner, the test is really an accelerated one.

Nevertheless, the term "accelerated" testing, ageing or weathering is usually intended to include those cases in which the natural features of sunlight, rain, frost etc., are simulated in an artificial manner by carbon arcs or mercury vapour lamps, water sprays, freezing chambers and the like, for these means lend themselves to securing an accelerated effect, which is important to industry in saving time. Indeed, in the past, one of the greatest hindrances to rapid advance in the paint and varnish industry has been the lack of any suitable method of quickly determining the value of, for example, a new medium. The difficulty still exists to some extent, in spite of the fact that the determination of the performance value of paint films, both by natural weathering and by tests in which conditions more drastic than normal exposure are produced artificially, is an every-day procedure. The problem lies partly in devising the most suitable form of accelerated test but mainly in interpretation. To be entirely satisfactory it is essential that all such tests shall quickly yield effects comparable with those obtained by natural exposure, and be reproducible at any time or place. They are not entirely satisfactory in this respect. At first sight one would expect that the time required for breakdown or for the appearance of some specific fault would bear a constant ratio to the time required to bring about a similar condition by means of natural exposure. Ideally this would be the requirement of such a test, but it is not possible to reproduce changing climatic conditions, or to intensify concurrently the various factors operating. However, an artificial weathering treatment can be constant in all relevant characteristics, whilst natural weathering is subject to marked variability from place to place and from time to time. Comparisons between natural and artificial weathering tests can never be reduced to arithmetic and disappointment is inevitable if too much importance is placed upon this desire for a definite time ratio. Nevertheless, provided the work is carried out with discretion on a strictly comparable basis—that is, similar materials should be compared with one another and with a material of which the real everyday performance value is known—then accelerated testing work can be quite valuable.

So far the reference to accelerated weathering has been mainly concerned with the simulation of the atmospheric influences such as would be expected to operate on paint applied to the exterior of a house or to a bridge. These influences promote changes in the paint films, both physical and chemical in character, until the material is no longer functioning as it should, when it is said to have broken down. The manner in which tests are devised to promote and to control the above described changes will be discussed later. Here it is necessary to point out that modifications of the parent test scheme are required to deal with special cases. Thus, paints intended for use as anti-rusting paints, anti-fouling paints (for use on underwater structures and on ships' bottoms), paints to withstand chemically polluted atmospheres, paints to withstand sea-water or salt contact (as with salted hides), paints to withstand attack by micro-organisms, paints suitable for application to pipes which have to remain buried for long periods in different types of earth, paints specially suitable for concrete, paints which will withstand tropical heat and rainfall alternating rapidly, etc., must all be regarded as special cases and special methods must be devised to deal with them.

The performance value of bituminous roofing felts, artificial leathers as used for motor-car hoods, japanned leather as used for patent leather shoes, must be judged by noting the change due to exposure brought about in those physical properties of the material which will be brought under review in use as, for example, loss of stretch, cracking on bending, and partial failure of adhesion and similar defects.

General Requirements of Weathering Tests.—The basis of accelerated weathering tests of a general character (apart from considerations which must arise when special features must be developed for specific purposes) is a cycle of artificially developed deteriorating agencies simulating the action of the weather. The simulation of climate in a laboratory test is obviously a complex matter and any apparatus devised for the purpose must be very flexible in use and capable of being adapted to a variety of conditions. The mechanical form of the apparatus will be determined by the appreciation of the nature of the different agencies which constitute and control the weathering effect : natural sunlight (a very variable factor) can be replaced and intensified, particularly in respect of ultra-violet radiation, by mercury vapour lamps and carbon arcs; artificial rain can be produced by a spray ; temperature changes, which may extend from tropical heat to heavy frost, can be provided easily.

The changes brought about in paint films by weathering may be considered as disruption due to chemical effects such as oxidation, disruption due to physical causes through inability of the film to withstand the strains induced by temperature variations, and wearing away by erosion. It is usual to consider the abrasion resistance and the hardness of films, which really determine the erosion factor, independently of the ordinary accelerated weathering test. Chemically the most important factors are the effect of moisture and the photochemical changes promoted by light and ultra-violet radiation ; physically, temperature changes and alternations of humidity are responsible for the setting up of stresses (causing unequal expansion and contraction either in different parts of the film or between the film and its support), which ultimately overcome the elasticity and tensile strength of the film. All these factors operate and ultimately cause film-breakdown, but the relative importance of the influences at work is not established. For example, much effort has been applied to the problem of determining which wave-lengths of ultra-violet light are most deleterious. It is fairly certain that the most effective radiations are below about 4,000Å, and probably at a maximum between 2,510 and 3,500Å. It is also possible to set up some degree of correlation between the rate of deterioration and the absorption bands of particular paint materials, but on balance it would seem better to retain the whole spectrum rather than a small part of it in accelerated testing work. In the matter of temperature control, it is the fact of change, the extent and frequency of change of temperature, much more than the actual temperature itself, which determines the rate, extent and nature of the deterioration of the film.

Breakdown of the film may become manifest by the loss of binding qualities in the medium and the consequent detachment of pigment at the film surface known as *chalking;* or minute cracking or *checking* may appear as the result of insufficient film elasticity. Insufficient bond between paint film and support may cause failure to resist the shearing forces set up in the plane of the film as the result of temperature changes, and show as a loss of adhesion and peeling of the paint film.

Water alone may not appear to have any serious effect on the film, but water exposure followed by light is severe and water and light together rapidly promote surface disintegration. The lower the moisture content of the film the less destructive will be the action of light. Alternations of humidity will affect the degree of water adsorption and the permeability characteristics of the film. The consequential stresses set up in the film between its different parts or between film and support will aggravate similar stresses due to temperature and together these stresses may rapidly cause fracture of a film, especially if it has been weakened by photochemical or chemical action. On the other hand the changes brought about in the elastic properties of a paint film under test may develop in a manner similar to that associated with fatigue in metals produced by cold working.

The effect of subjecting the test panels to refrigeration at regular intervals is not as a rule striking, but some types of breakdown can be further accelerated without destroying their fundamental characteristics. Much depends of course, on the sequence, *i.e.* whether refrigeration follows water immersion or light exposure, and on the elastic properties of the film. The more severe the temperature change and the less the natural elasticity of the film, the greater the effect of refrigeration but, as already suggested, it can often be omitted without great loss. Apparently nothing is gained by heavy freezing, so that a daily exposure of 2 hours in a cabinet working at 25°F. is sufficient for general practical purposes.

Very little more can be said as to the relative importance of the effects contributed by the different active agencies—they are all important and must be included in an exposure cycle. Obviously the details of the cycle of treatment, *i.e.* the sequence and time of contact with each active agency, will still leave large possibilities of variations in the results obtained.

APPARATUS.—Various forms of apparatus have been described for exposing test panels to convenient operating cycles, the object being the maximum degree of acceleration with the minimum departure from the results of standard or natural exposure.

Much experimental work has been carried out on this subject in America, England and, to some extent, in Germany. A description of a practical apparatus for carrying out accelerated weathering tests on paints and varnishes is given by Muckenfuss (Ind. Eng. Chem. 1913, **5**, 7, 535 ; Proc. Amer. Soc. Testing Materials, 1914, **14**, 11, 361) who used air-tight cylindrical boxes (7 ft. diam.×4 ft. high) with the weathering forces situated on the axis : rain was simulated by a whirling garden spray, sunlight by means of mercury vapour and tungsten lamps in combination, cold weather by admitting outside air at night, and ventilation by a fan while the lamps were in operation.

Of the more recent American work, that of H. A. Nelson and his collaborators of the New Jersey Zinc Co., Ltd. (H. A. Nelson and F. C. Schmutz, Ind. Eng. Chem. 1926, **18**, 1222 ; *see also* Proc. Amer. Soc. Testing Materials, 1922, **22**, 485 ; 1924, **24**, 920 ; 1926, **26**, 563) invites attention on account of its systematic and thorough character. Nelson uses a cylindrical tank in which a quartz mercury lamp 30 in. long is suspended axially at a distance of approximately 24 in. from the panels, which are hung round the walls. A water spray and an atomiser are fitted in order to obtain the effects of humidity. The usual procedure is to expose the panels to radiation from the lamp for a period of approximately 18 hours a day, 24 hours on Sunday, a total during the week of 92 hours with the water spray and 40 hours without. Later developments include a daily exposure of the panels in a refrigerator at 20°-25°F. for a period of 2½ hours, and the use of an oxygen-enriched atmosphere in the exposure tank.

H. A. Gardner of the Institute of Paint and Varnish Research, Washington, has described several forms of weathering apparatus. His original apparatus (*see* Amer. Paint and Varnish Manuf. Assoc., Circ. 226) consists of a rotating cylindrical drum, 5 ft. in diameter, on the outer face of which panels are carried. The drum is rotated in a vertical plane, as it were on edge, at the rate of two revolutions per hour, and the panels pass in turn under the action of a water spray, a mercury-in-quartz lamp, a battery of 12 electric heating lamps and, finally, ice water or air cooled below 0°C. He concluded after two years' experimenting that although some useful information could be obtained with this apparatus as to the durability of protective films, he could improve the speed of the breakdown by locating the source of radiation at the centre of the wheel, so that the panels would be irradiated continuously instead of only intermittently. In a later publication (Amer. Paint and Varnish Manuf. Assoc., Circ. 323) Gardner describes an entirely different type of weathering equipment, consisting of a galvanised iron tank 52 in. in diameter and 25 in. deep, around the inner face of which the panels are supported and inside which a rotating frame is suspended. This frame is fitted with four arms, two of which carry enclosed carbon arc lamps and the other two carry fine water sprays. The speed of rotation in a horizontal plane is two revolutions per hour. Apparently the intention is to run this apparatus continuously without any systematic refrigeration of the panels, but where necessary to apply a small cooling chamber to the back of the panels while they are still in the tank. In the cooling chamber a mixture of either salt and ice or, for lower temperatures, acetone and solid carbon dioxide is used. It is claimed that results obtained in this apparatus approximate to those from natural exposures.

P. H. Walker and E. R. Hickson of the Bureau of Standards describe an apparatus (*see* Bur. Stand. J. Res. 1928, **1**, 1) in which panels are supported in a cylindrical drum, 30 in. in diameter and 15 in. high. In the drum an enclosed carbon arc carrying 13 amperes is suspended axially ; water sprays are fitted in order to obtain the effects of humidity either intermittently or continuously. As the drum usually makes three revolutions per hour with one water spray, each panel receives a water spray for about 40 seconds once every 20 minutes during the test. Walker and Hickson originally included refrigeration but later considered it to be unnecessary ; they also included exposure to ozone as part of the weathering cycle but have since discontinued this practice.

These American forms of weathering apparatus based on the enclosed carbon arc are manufactured by the Atlas Electric Devices Co. of Chicago under the name *Weather-Ometer* and described in B.P. 283539. Numerous references are found in the German literature from 1906 onwards to the effect of mercury vapour light in comparison with sunlight on various materials but mainly on dyes and coloured products. M. Schutz (Farben-Ztg. 1927, **32**, 2128) describes the different types of artificial weathering apparatus used in Germany. In the main German workers have combined such apparatus with severe chemical treatment by immersion in baths containing weak solutions of acids, alkalis and salts. In the apparatus used by the Chemisch-Technische Reichsanstalt, the test panels are carried on a rotating framework by which they are dipped into baths containing such solutions for 20 minutes and then exposed to the radiation from a quartz mercury vapour lamp for 40 minutes in each hour. Ritter (Korrosion und Metallschutz, 1929, **5**, 66) describes apparatus in which the panels are carried on endless chains, arranged so that the films can be exposed to the action of concentrated salt solutions and to ultra-violet and/or daylight radiations under variable conditions of temperature and humidity ; arrangements are also made so that these destructive agencies can be employed in any desired combination. Ritter claims that with this treatment a period of 33 to 64 hours is generally sufficient to *determine the utility of any particular protective coating. It must be stated, however, that this type of mixed test is not generally approved even in Germany.*

It is known that in England for many years past individuals have devised and used various forms of accelerated weathering apparatus. The subject was studied at the Paint and Varnish Research Association, Teddington, Middlesex, in 1927 and, as a result, the conclusion was reached that the most suitable form of apparatus must depend upon a carbon arc assembled after the manner of the Bureau of Standards apparatus described above which was developed concurrently. Since that time there has been no marked development in design of weathering apparatus except a tendency towards larger units and simplified procedure. Many kinds of coating materials have been tested in this type of apparatus and, in general, although precisely the same defects may not develop in precisely the same manner or at the same time relative to the total life of the films, yet, by this means a series of paint materials may be placed in the order of external durability. The treatment may be continued until complete breakdown of the test material occurs, or until some specific defect develops but more usually the appearance of the panels is reported upon at the end of 500 or 1,000 hours or some other arbitrarily chosen period.

Accelerated weathering equipment is often made suitable for use with an atmosphere enriched by oxygen addition. It has been shown (H. A. Nelson and F. C. Schmutz, Ind. Eng. Chem. 1926, **18**, 1222) that without altering the relative order of performance merit of a number of paint films, the rate of destruction may be doubled by enriching the air in the equipment to contain 30% oxygen by volume.

Atmospheres contaminated with corrosive gases may also be used, but such are not usually included in weathering cycles for general use, although they may be of value in studying the resistance of coating compositions to specific breakdown conditions. Spraying with salt water may be used for the assessment of paint films for use near the sea ; this variation may be inserted into the normal accelerated weathering cycle or it may be carried out as a separate test. No elaborate arrangements are necessary, it usually being sufficient to suspend the panels in a cupboard or small room into which a mist of salt water is projected. In this way results which are arrived at by exposure in salt-laden air, such as in racks mounted over the surface of the sea, may be obtained quickly.

The only essential difference between the various forms of equipment described is found in the sequence and time ratio of the different steps, the temperature change induced by refrigeration when used, and in the choice of an artificial illuminant. This latter is limited by various practical and economic considerations to the quartz mercury vapour lamp and the carbon arc ; the former proves the more rapid in inducing paint film breakdown, but, as would be expected from considerations of energy relationships, the difference between natural and mercury arc exposure is more exaggerated than that between natural and carbon arc exposure. It has been shown (*S. L. Clark and H. L. Tschentke, Ind. Eng. Chem. 1929*, ***21***, *621) that* paint vehicles are very absorbent in the lower range of wavelengths below those of solar radiation in which the mercury-in-quartz arc radiation is rich. Furthermore, reactions so induced in the film may be quite different in character from those experienced in normal solar exposure. Another drawback to this type of arc is the opacity gradually induced in the quartz and the variable nature of the output.

The carbon arc radiation, although approximating closely to solar radiation, is by no means identical with it and photochemical changes induced in a film therewith will not necessarily be similar in the two cases. There are, however, no difficulties with the carbon arc arising from changing output with age, and it is rapidly replacing the mercury lamp for accelerated weathering equipment, notably in America; the carbon arc was always most favoured in England.

High amperage carbon arc systems are sometimes used to provide more intense radiation and the acceleration gained is very considerable although it is found that the film breakdown promoted is rather different in character from that induced by the normal carbon arc.

The use of iron-cored carbons and similar devices to increase the amount of ultra-violet radiation introduces the same difficulties as the mercury quartz lamp and as a rule is not to be recommended.

Results Obtained.—In carrying out artificial weathering tests it is important always to include material of known service characteristics for then it is usually possible to draw useful conclusions and to avoid many cases of serious discrepancy between the results of the artificial and the natural weathering tests which would be otherwise inevitable. It is unfortunate that users commonly expect the destructive action of an artificial weathering treatment to be expressed as a constant ratio to the summation of natural weathering agencies. This is an unreasonable demand and in the absolute sense is impossible ; with discretion a close approximation may be made as to the likely performance of a product under natural conditions by examination of its behaviour under established artificial conditions, but discrepancies cannot fail to occur if comparative tests are based on the conception that the matter is one of mere arithmetic. However, the ratio which perhaps represents most closely the average of the widely scattered ratios for different materials and conditions is that one 24-hour day of the artificial cycle is equivalent to from 2 to 4 weeks of " average " natural exposure according to the age of the film when exposure commences, the normality or abnormality of the season, and the nature of the product. A more satisfactory index of performance of artificial weathering is to state the average life in hours of typical coatings which may range from 200 hours up to 2,000 hours according to the rigour of the test cycle and the type of material under examination.

Pigmented products generally last better than the corresponding unpigmented clear medium, and this effect is maintained under the accelerated test. Poor quality coatings or unsuitable paint mixes are quite easily disclosed by accelerated weathering which is also particularly valuable for revealing incongruous undercoating systems or other forms of incompatibility between coats.

The differences between results from wood and from metal panels are often much greater than is supposed. There are several reasons for these differences. Wood adsorbs some of the medium from any paint or varnish applied to it, metal does not. The foundation produced by a given undercoating on wood will differ, therefore, in physical properties from that produced on metal, with the result that there will be a different relationship with the finishing coat. A more important cause of distinctions is that wood adsorbs moisture and expands and contracts considerably with changes in water content. Not only, therefore, do the moisture relations of a film on wood differ from those of a similar film on metal but, in addition, powerful distorting forces are introduced by the wood and not by the metal. Wood, moreover, is a much poorer heat conductor than metal and the effects of temperature changes in the surroundings are likely to be more severe in the film on wood. During a heat exchange between a panel and its surroundings by conduction or radiation a film on a metal panel will have a smaller temperature gradient from back to front than will a similar film on a similar wooden panel. Stresses due to differential expansion from this cause will, therefore, be less severe on metal than on wood. But for one undesirable feature the more severe action of wood on a film might be regarded as an advantage for many tests because it leads to more rapid breakdown and an earlier conclusion. This feature is the variability of wood.

Of the metals which are available ordinary iron or steel would be the most suitable were it not for the fact that good films are often destroyed by the growth of rust beneath them. Aluminium and zinc surfaces appear to have poor adhesion for paint and varnish films. Monel metal is better, and stainless steel appears to be without effect on paint or varnish films and is unaffected by them.

A further feature which has a most important influence on the life of a paint or varnish film, and, therefore, on the conclusions to be drawn from a test, is the treatment it receives during the first few days after spreading.

In the following table are given the times at which first signs of breakdown were noted on three sets of panels coated with the same series of paints and exposed to a standardised accelerated weathering treatment after periods of 2 hours, 2 days, and 30 days respectively.

Effect of duration of drying on life of a set of paints exposed to artificial weathering.

Paint No.	Time of breakdown, when test began after		
	2 hours.	2 days.	30 days.
A	422 hours	413 hours	1,300 hours
B	69 ,,	208 ,,	1,160 ,,
C	320 ,,	277 ,,	1,300 ,,
D	69 ,,	136 ,,	860 ,,
E	158 ,,	113 ,,	300 ,,

The order of merit of the paints is the same whether dried for two days or for thirty days, although the longer drying period gives a much longer life. The series exposed after only two hours, however, gives discordant and unreliable results because the exposure is an abnormal interference with the half-completed process of film formation.

For systematic testing therefore a standardised drying routine must be adopted. The rate and mechanism of drying varies from film to film and the ideal method would be to dry to completion, if such a concept may be employed. Time seldom allows of this and, as a compromise, a period of five days at 25°C. and 60% humidity is given as reasonable for the drying of panels to be tested by accelerated weathering.

FUTURE DEVELOPMENT OF WEATHERING TESTS.—Many technologists are now working on the principle of combining a form of weathering test, accelerated or otherwise, with other more precise tests suitable for carrying out on the film, such as resistance to bending, extensibility, hardness, and the like (*see* Schuh and Theurer, "Physical Evaluation of Finishes," Ind. Eng. Chem. (Anal. Ed.), 1934, **6**, 91).

SPECIAL TYPES OF ACCELERATED TESTS.—There are ways of estimating the value of paint and similar materials without the overall weathering test above described, which depend upon :

(*a*) the examination of the film properties known to be affected by particular conditions, such as mechanical strength, elasticity, water sensitivity and colour fading, though consideration of the latter is not included in this article ;

(*b*) methods of rapidly promoting specific film defects to which particular materials are prone, such as accelerated tests for blistering, wrinkling, etc.

These special tests can be linked, at least to some extent, with the general weathering test, and as a result some appreciation of the value of paint films can be given in a much shorter time than is usually required for an exposure test.

THE GALVANIC COUPLE TEST.—In this test (W. P. Digby and J. W. Patterson, "Accelerated Tests of Paints for Steelwork," The Engineer, June 8 and 15, 1934), the panel carrying the material under test is made a part of a simple voltaic cell which functions if the paint film is not complete ; the passage of current accelerates further breakdown.

Briefly, and in its latest form, the apparatus consists of :

(*a*) a steel plate coated on each side with the protective material it is desired to test ;

(*b*) two graphite electrodes placed one on either side of the painted steel plate (*a*) ;

(*c*) a metal container with an insulating lining made in two halves bolted together. The steel plate (*a*) forms a diaphragm or partition between the two halves of the container ;

(*d*) a multi-way switch for each cell ;

(*e*) connecting leads between the electrodes and the switches and between the switches and the galvanometer ;

(*f*) a portable galvanometer with a series of resistance shunts.

The apparatus is used in the following manner. The paint to be tested is applied to the steel plate by brushing, spraying or dipping, the paint being of normal consistency. The halves of the metal container are bolted together with the steel plate between them. This gives two compartments; one of the graphite electrodes is placed in each compartment. Into each compartment is then poured the electrolyte selected with reference to the projected use of the paint ; thus in an industrial area suitable electrolytes would include local tap water, a centi-normal solution of sulphuric acid and a chloride solution containing 2½% sodium chloride. Paints required for marine use should be tested in 100% sea water and also in brackish waters. For testing the internal coating of tanks containing alkaline fluids, a centi-normal solution of caustic soda is generally used.

A perfect paint—if there were such—would not only be impermeable but would remain so indefinitely. Before visible breakdown is evident in the shape of rust spots or of wide rusty areas, there is a progressive increase in the galvanometer reading as the insulating quality of the paint film falls. This type of test is extremely valuable where the contemplated conditions of exposure and use of the material justify it.

TESTS FOR BLISTERING AND DEFECTS ARISING OUT OF WATER PERMEABILITY AND ADSORPTION.—The actual passage of moisture through a detached film may be measured by a number of methods, usually involving the suspension of the film between a desiccating chamber and one containing saturated water vapour. The gain in weight of the desiccating material is directly related to the permeability of the film (R. J. Wray and A. R. Van Vorst, Ind. Eng. Chem. 1933, **25**, 842–6).

The blistering of paint films causes a good deal of trouble on wood and plaster and arises because the moisture brought to the surface by heat or sunlight is unable to escape through hard and somewhat impermeable paint films. An accelerated test may be made with a metal box kept half-filled with water and maintained at 60°C. The wooden panels carrying the paint films to be tested on the upper side serve as a lid to the metal box. Moisture penetrates through the wood and in paints likely to give subsequent trouble will cause blistering in 24 hours.

If it is desired to avoid defects of this character, consideration must be given to the problem of bringing prepared wooden panels to equilibrium moisture content by suitable storage before painting (*see* F. L. Browne, Ind. Eng. Chem. 1933, **25**, 835 ; *also* R. J. Wray and A. R. Van Vorst, *ibid.* 842).

Water adsorption by varnish films may cause *whitening* or *milking* of the surface ; this condition is an optical result of the presence of fine water droplets in the film. A predisposition to this condition is revealed by immersion of dried films in water for 24 hours, after which it is usual to redry the material and examine it again. These tests will show whether the tendency to adsorption of water is serious enough to cause wrinkling of the film or loss of adhesion to the support.

The hazy surface appearance sometimes met with in paint and varnish finishes is often evidence of another type of moisture attack. *Bloom* is often, but not always, an exudation from the surface of the material. The " bloom " referred to here as the result of moisture attack is a physical distortion of the surface due to condensation before the film is strong enough to resist. Again, if a paint or varnish film is strongly water-attractive it is not unusual to find a film-like deposit being formed in the surface which results in a loss of gloss ; this condition is also known as " bloom," and is due to the adsorption of ammoniacal salt impurities from the atmosphere. Accelerated tests for defects of this kind obviously take the form of exposing the paint films during the early stages of drying to a suitable atmosphere of high humidity.

TESTS FOR WRINKLING AND WEBBING DEFECTS.—A properly adjusted paint or varnish composition should flow out to a smooth film on the surface to which it is applied without brushmarks or other defects. Certain types of varnish are inclined to show the defects of *wrinkling* and *webbing* under unfavourable conditions of application. In the British Standard Specifications for Varnish (*see* B.S.S. No. 256 for Interior Oil Varnish) an accelerated test for this condition is described :

" The material shall not ' web ' or ' frost ' when tested in the manner described.

" Glass plates (*e.g.* microscope slides) shall be coated on one side with the varnish to be tested and drained vertically for half an hour. The plates shall then be placed upon strips of cardboard of the same size and dried on the central shelf of a suitable oven (see below), care being taken not to cover up the perforations in the shelf.

" A suitable oven is a copper air oven 6×6×6 in. (approx. 15×15×15 cm.) having a hole 1·0 to 1·25 in. (approx. 2·5 to 3·0 cm.) in diameter in the middle of its floor and containing a perforated copper shelf placed centrally. At the top of the oven are two tubulures about 0·5 in. (approx. 1·25 cm.) in diameter, one of which is left open while the other is furnished with a cork through which passes a thermometer with its bulb reaching to the central shelf.

" A small burner, 0·16 in. (approx. 0·4 cm.) in internal diameter, burning coal gas and giving a luminous flame 0·5 in. (approx. 1·2 cm.) high, shall be placed underneath the hole in the oven floor at such a distance that the tip of the flame is about 3·25 in. (approx. 8 cm.) from the plane of the floor. By this means with an outside temperature of about 14°C. (57°F.) a temperature of about 38°C. (100°F.) will be maintained at the shelf of the oven."

TESTS FOR HARDNESS, EXTENSIBILITY AND STRENGTH.—The properties of a paint or varnish film which are related to toughness and general resistance to abrasion and other mechanical breakdown influences are of importance in determining its suitability for application to certain types of surfaces. They are particularly important where large dimensional changes may be experienced and where mechanical attack may be expected. A number of tests are applied in order to determine in a short time the expected mechanical resistance of films in use.

Hardness may be assessed by the standard Air Ministry scratch hardness test (Air Ministry Specification, D.T.D. 260, Appendix II) in which a loaded hemispherical steel point of 1 mm. diameter is passed over the film. The load required to break through the film to the metal panel on which it is painted may be determined, or the scratch produced under a given load examined. The results obtained are useful, but the possibility of flaking in brittle films must not be overlooked.

For the measurement of the effects of mechanical abrasion a direct sand abrasion method is used. A stream of sand is allowed to fall from a suitable reservoir through a vertical tube into which compressed air is introduced by means of a T piece, on to a metal panel set at 45° and carrying the composition under test. The effects of such abrasion are at first a dulling of the film followed by a gradual wearing away or, after a certain amount of wear, large blisters may form, which on breaking expose the base metal of the panel in large patches. The end point is usually quite definite and the resistance is assessed by the mass of sand required to abrade the film so as to expose a small patch of metal.

Direct tests of the strength of detached films may be made as for thin papers ; the usual procedure for this type of test is to hold a detached film in a vertical plane between two clamps, the lower of which is attached to a vertical spiral spring and the upper to a device by which it can be made to rise at a constant speed, taking the film and the lower clamp with it. In this way a tension is applied to the film which stretches accordingly. The extension is measured by the increased distance between the clamps ; and the load by the extension of the spring. Extensibility is determined in this way and the load may be increased to break the film and thus determine the tensile strength.

It is possible to correlate tensile strength and elastic properties with durability ; low tensile strength and small extensibility will give rise to early failure.

Ideally any such tests of strength should be made on films carried on the particular support required and the observed effects allocated to film or to support. This is generally impracticable and it is more convenient and, in so far as the film may be judged on its own merit, a more satisfactory procedure to carry out extensibility tests on detached films usually prepared by flotation of the paint or varnish on a mercury surface. The method has been used successfully for general assessments of materials and for particular studies such as an examination of the effects of driers on the strength of varnish films (F. Wilborn, F. Wachholtz, O. Walther, and H. Ulrich, Farben-Ztg. 1932, **37**, 1120) and for the classification of plasticisers for behaviour in nitrocellulose lacquers (G. G. Jones and F. D. Miles, J.S.C.I. 1933, **52**, 251T).

LIST OF REFERENCES ADDITIONAL TO THOSE QUOTED IN TEXT.

H. A. Gardner, " Physical and Chemical Examination of Paints, Varnishes, Lacquers, Colors," 7th ed., 1935, Chap. 13, Inst. of Paint and Varnish Research, 2201, New York Avenue, Washington, D.C.

H. A. Gardner and G. G. Sward, " Accelerated Testing Equipment," Amer. Paint and Var. Manuf. Assoc. Circ. 358.

J. K. Hunt and W. D. Lansing, " Coating Composition Films," Ind. Eng. Chem. 1935, **27**, 26.

V. G. Jolly, " The Accelerated Weathering of Paints and Varnishes," J. Oil and Colour Chemists' Assoc. 1933, **16**, 366 ; *also* J.S.C.I. 1933, **52**, 329T.

S. A. Levy, " Development of a Photo-Chemical Test for quickly rating the Durability of Varnishes," Amer. Paint and Var. Manuf. Assoc., Circ. 410.

F. C. Schmutz and D. L. Gamble, " Studies of Destructive Light Sources for use in Accelerated Weathering Systems," Ind. Eng. Chem., Anal. Ed. 1929, **1**, 83.

Report of Sub-Committee VII on " Accelerated Tests for Protective Coatings," Proc. Amer. Soc. Testing Materials, 1929, **29**, Part I, 346.

J. H. Wilson, " A New Test for Predicting the Durability of Varnishes," Bur. Stand. J. Res. 1931, **7**, 73.

L. A. J.

AGMATINE (*α*-amino-*δ*-guanino-*n*-butane)

$$NH{:}C(NH_2)NH{\cdot}[CH_2]_4{\cdot}NH_2,$$

is obtained by heating herring spawn with dilute sulphuric acid under a pressure of 4 atmospheres. It is formed from arginine,

$$NH : C(NH_2)NH{\cdot}[CH_2]_3{\cdot}CH(NH_2)COOH,$$

by the loss of CO_2.

AGNOLIN, Lanolin (*q.v.*).

AGONOL. Trade name for santalyl benzoate, a substitute for santalol in medicine.

AGROPYRUM. *Triticum. Couch grass.* The rhizome of a weed *Agropyron repens* (Fam. Gramineæ). It contains a carbohydrate triticin which resembles inulin, dextrose, mucilage, mannitol and inositol. A demulcent diuretic.

AGURIN. Trade name for the addition product of theobromine-sodium and sodium acetate, $C_7H_7N_4O_2Na,C_2H_3O_2Na$. Diuretic.

AGUTTAN. Trade name for the salicyl ester of 8-hydroxyquinoline (*oxine*),

$$C_6H_4(OH)COOC_9H_6N,$$

m.p. 107°. Used in the treatment of gout.

AICH METAL. An alloy (Cu : Zn : Fe = 60 : 38·5 : 1·5) patented by J. Aich in 1860 for use as sheathing for ships.

AILANTHUS SILK. *Ailanthus glandulosa*, the Chinese sumach tree is grown in France for its leaves on which silkworms are fed. The silk of this name derived from a silkworm *Attacus atlas* resembles tussah.

AIROFORM. *Airogen. Airol.* Trade names for bismuth oxyiodogallate,

$$C_6H_2(OH)_3COOBi(OH)I.$$

Substitute for iodoform in the treatment of wounds.

AIROGEN *v.* AIROFORM.

AIROL *v.* AIROFORM.

AJACINE. An alkaloid, $C_{15}H_{21}O_4N,H_2O$, m.p. 142°–143°, in the seeds of *Delphinium ajacis* (O. Keller and O. Völker, Arch. Pharm. 1913, **251**, 207; J.C.S. 1913, A. i, 642)—*v.* DELPHINIUM ALKALOIDS.

AJOWAN OIL. *Ptychotis oil.* The oil distilled from the fruits of *Carum ajowan* (Bentham and Hooker), N.O. Umbelliferæ, and *Ptychotis ajowan* (D.C.). It is cultivated in India and also grows in Persia and Afghanistan. Yield of oil 3 to 4%.

Character.—Sp.gr. 0·900–0·930, opt. rot. +1° to +2°. Soluble in 3 vols. 70% alcohol. Contains thymol 35 to 50%, α-pinene, dipentene, *p*-cymene, γ-terpinene and phellandrene. This oil was formerly the chief source of thymol, but this is now usually manufactured from piperitone. C. T. B.

AKARDIT (*as*-diphenylurea),

$$NH_2{\cdot}CO{\cdot}NPh_2,$$

is used as a gelatiniser and stabiliser in connection with smokeless powders (*see* EXPLOSIVES). H. S.

AKROCHORDITE. Hydrous basic arsenate of manganese and magnesium,

$$Mn_3As_2O_8{\cdot}MnOH{\cdot}MgOH{\cdot}5H_2O,$$

found as small reddish-brown spherical or warty aggregates in manganese ore at Långban, Sweden. The optical characters indicate monoclinic symmetry. Named from ἀκροχορδών, a wart (G. Flink, Geol. För. Förh. 1922, **44**, 773). L. J. S.

AKTIVIN. A crude chloramine T placed on the market under the name "Aktivin"; is intended for large-scale disinfection.

AKTOPROTEIN. Trade name for a 4% solution of fat-free casein. Used in protein therapy.

AKUAMMINE *v.* YOHIMBOA ALKALOIDS.

ALABANDITE. Manganese sulphide (MnS).

ALABASTER. (*Albâtre*, Fr.; *Alabaster*, Ger.) A fine-grained, massive and marble-like form of the mineral gypsum ($CaSO_4{\cdot}2H_2O$), occurring as seams and lenticular masses in deposits of coarser gypsum rock. Specific gravity 2·30–2·33. Being soft (hardness 2) it is more easily worked than marble, and it is much used for interior decorative stone-work and for various small ornamental objects. Veined and mottled varieties have recently been much used as inverted bowl-shaped shades for ceiling electric lights. The material has been quarried at Chellaston in Derbyshire, Fauld in Staffordshire and near Newark in Nottinghamshire, where it occurs in beds of Keuper Marl of Triassic age. Occurrences in the Eden valley in Westmorland are of Permian age. A snow-white alabaster occurring as nodules in limestone and marls of Tertiary age in the Volterra district in Tuscany has long been used for carving, the centre of the industry being at Florence. Large deposits are worked at several places in Nova Scotia and New Brunswick and in the United States one locality in Iosco County, Michigan, has the name Alabaster.

The harder varieties of alabaster are worked with the same tools as marble, smoothed with pumice, polished with a mixture of chalk, soap and milk, and finished by friction with a flannel. Softer material may be turned or fashioned with rasping tools, smoothed with dried shave grass, then rubbed with a paste of putty powder and polished with talc. In order to produce a rather greater degree of opacity and a resemblance to marble ("marmo di Castellina"), the carved objects are immersed in a bath of water which is gradually brought up to nearly the boiling-point. The material may be coloured by heating it to about 90° or 100°, and then dipping it into solutions of metallic salts or dyes. A good imitation of red coral ("alabaster coral") is so produced.

See Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, Gypsum and Anhydrite, vol. 3, 1915, 2nd ed., 1918; W. A. Richardson, Min. Mag. 1921, **19**, 196; L. H. Cole, "The Gypsum Industry of Canada," Canada, Mines Branch, 1930, no. 714; H. Ries, "Economic Geology," 6th ed., New York, 1930.

The name alabaster has also been applied, especially in ancient times, to another mineral, namely calcite (calcium carbonate) in the form of onyx-marble or stalagmitic marble. Most, though not all, of the carvings of the ancient Egyptians are in this material. Pliny records that *alabastrites* was quarried near the city of Alabastrum in Egypt. The two kinds are readily distinguished by the action of acids and by their difference in hardness. Sulphate alabaster can be scratched by the finger-nail, while carbonate alabaster cannot. The latter is, however, easily scratched by a knife point. L. J. S.

ALACREATINE *v.* CREATINE.

ALAITE. Hydrated vanadic oxide,

$$V_2O_5{\cdot}H_2O,$$

found as blood-red, mossy growths with silky lustre at Tyuya-Muyun in the neighbourhood of the Alai Mountains in Fergana, Russian Central Asia. The uranium and vanadium deposits mined at this locality consist of vanadates of uranium, calcium and copper, occurring as impregnations in a coarse-grained Devonian limestone (K. A. Nenadkevič, J.C.S. 1909, **96**, ii, 411). L. J. S.

ALAMOSITE. A lead silicate $PbSiO_3$ found near Alamos, Sonora, Mexico; analogous to wollastonite $CaSiO_3$ in form, habit and composition. It occurs as radiated aggregates of minute colourless transparent fibres, which give a snow-white appearance to the mass (Palache and Merwin, Amer. J. Sci. 1909, **27**, 399; J.S.C.I. 1909, **25**, 606). L. J. S.

ALANINE, *α-Alanine, α-aminopropionic acid* $NH_2{\cdot}CHMe{\cdot}CO_2H$, contains an asymmetric carbon atom, and the dextro, lævo-, and racemic isomerides are known. *d*-Alanine is one of the decomposition products of a large number of proteins; together with a glucoprotein $C_7H_{14}O_4N_2$ it forms 51% of the product obtained by the hydrolysis of legumin of peas (Bleunard, Ann. Chim. Phys. 1882 [v], **26**, 47), and is formed to the extent of 21% from silk fibroin (Weyl, Ber. 1888, **21**, 1529; Fischer and Skita, Z. physiol. Chem. 1901, **33**, 177; Johnson,

J. Amer. Chem. Soc. 1916, **38**, 1392). It is found in yeast protein (Neuberg, Woch. Brau. 1915, **32**, 317), and in "Zurdon's" meat extract (Z. physiol. Chem. 1913, **83**, 458). (For the methods of separating alanine from the other hydrolytic products of protein, *v.* art. PROTEINS.) *r*-Alanine is prepared synthetically by the action of hydrochloric acid on the aminonitrile $NH_2\cdot CHMe\cdot CN$, produced by the interaction of aldehyde ammonia and hydrogen cyanide (Strecker, Annalen, 1850, **75**, 29); or, together with α-aminopropionitrile hydrochloride, when ammonium chloride, potassium cyanide and acetaldehyde interact in equimolecular quantities in aqueous solution (Zelinsky and Stadnikoff, Ber. 1908, **41**, 2061); by reducing α-nitrosopropionic acid with tin and hydrochloric acid (Gutknecht, Ber. 1880, **13**, 1116); or hydrolysis of α-triazopropionic acid (Curtius, J. pr. Chem. 1889 [ii], **38**, 396). It can be obtained from pyruvic acid by the simultaneous action of hydrogen and ammonia in the presence of colloidal palladium stabilised by starch paste (Aubel and Bourgel, Compt. rend. 1928, **186**, 1844). Alanine can also be prepared from ammonium pyruvate by the action of yeast. The yield is from 3–65% according to the yeast used (Fromageot and Desnuelle, Bull. Soc. chim. 1933 [iv], **53**, 541; Biochem. Z. 1934, **273**, 24).

Alanine crystallises in needles or sharp rhombic prisms, dissolves in 4·6 parts of water at 17°, or in 500 parts of 80% cold alcohol. For solubility and optical activity of r-*alanine*, *see* Pellini and Coppola (Atti R. Accad. Lincei, 1914 [v], **23**, 1, 144, from Chem. Zentr. 1914, **1**, 124). Its heat of combustion is 389 kg.cal. and heat of formation 135·2 kg.cal. (Berthelot and André, Compt. rend. 1890, **110**, 884). For quantitative estimation of the light absorbed by complex salts of alanine, *see* Ley and Hegge (Ber. 1915, 48, 70), and for the influence of neutral salts on the rotatory power of alanine, *see* Pfeiffer (Ber. 1915, **48**, 1938). The resolution of racemic alanine has been effected through the benzoyl derivative, which is separated into d-*benzoylalanine* (m.p. 147°–148°, $[\alpha]_D$ +37·13° in alkaline solution), and l-*benzoylalanine* (m.p. 150°–151° (corr.), $[\alpha]_D$ −37·3° in alkaline solution), by crystallisation of the brucine salt, and these yield on hydrolysis the corresponding optically active alanines; r-*alanine* decomposes at 264°–268° (Zelinsky and Stadnikoff, *l.c.*), at 293° (Fischer, Ber. 1899, **32**, 2451); d-*alanine* has $[\alpha]_D$ +9·55° in hydrochloric acid solution; d-*alanine* is unchanged when heated with strong hydrochloric acid (Abderhalden, Z. physiol. Chem. 1912, **82**, 167). Its aqueous solution is decomposed on exposure to sunlight (Ganassini, Giorn. Farm. Chim. 1912, **61**, 439; l-*alanine* decomposes at 297° and has $[\alpha]_D$ −9·68° in hydrochloric acid solution. r-*Alanine* is attacked by fermenting yeast (Ehrlich, Biochem. Z. 1914, **63**, 379). A cultivation of *Aspergillus niger* in an aqueous solution of *r*-alanine destroys about 10% of the dextrorotatory constituent, but *Penicillium glaucum* does not flourish in a 2% alanine solution. Resolution has been effected also by means of *d*-bromocamphorsulphonic acid (Colombano and Sanna, Atti R. Accad. Lincei, 1913 [v], **22**, 11, 292–298; Gazzetta, 1914, **44**, 1, 97) and by *d*-hydroxymethylenecamphor (Kipping and Pope, J.C.S. 1926, 494).

In its physiological action, *d*-alanine causes a rapid rise in the urinary nitrogen, most of the extra nitrogen being excreted on the same day; *l*-alanine is not decomposed quite so rapidly, but none of it is excreted unchanged (Abderhalden and Schittenhelm, Z. physiol. Chem. 1907, **51**, 323; compare, however, Sevene and Meyer, Amer. J. Physiol. 1909, **25**, 214); when given with lactic acid it causes an increase in dextrose elimination almost equal in amount to the theoretical yield (Dakin and Dudley, J. Biol. Chem. 1914, **17**, 451). After administering 20 grms. of *r*-alanine, 4·7 grms. of the β-naphthalenesulphonic derivative of *l*-alanine was recovered from the urine (Schittenhelm and Katzenstein, Chem. Zentr. 1906, i, 1279). When *d*-alanine is injected in the blood-stream it is rapidly absorbed, as very little can be detected in the blood or urine after a lapse of twenty minutes (Abderhalden and others, Z. physiol. Chem. 1907, **52**, 507; **53**, 113, 148, 251, 326; 1913, **86**, 478; and J. Biol. Chem. 1915, **20**, 539).

The importance of alanine as a final hydrolytic product of many proteins has led to an extensive examination of its derivatives in order to facilitate its detection and estimation (Abderhalden and Schmidt, Z. physiol. Chem. 1913, **85**, 143; Dakin and Dudley, J. Biol. Chem. 1913, **15**, 127; Chelle, Ann. Chim. Analyt. 1914, **19**, 67), and to determine the part it plays in the building up of the protein molecule. A short account of the more important of these derivatives is appended.

The *copper salt* $(C_3H_6O_2N)_2Cu,H_2O$ forms bluish-violet crystals readily soluble in water. The *nickel salt* $(C_3H_6O_2N)_2Ni,4H_2O$ forms blue crystals; these become anhydrous at 108°–110° and dissolve in 132 parts of water (Orloff, Chem. Zentr. 1897, ii, 192; Bruni and Fornara, Atti R. Accad. Lincei, 1904 [v], **13**, ii, 26). Complex salts are formed with heavy metals, *e.g.*

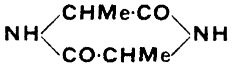
$$Cr(C_3H_6O_2N)_3Cr(C_3H_6O_2N)_2OH\cdot H_2O$$

(Tschugaeff and Serbin, Compt. rend. 1910, **151**, 1361; Ley and Winkler, Ber. 1912, **45**, 372; Ley and Ficken, Ber. 1912, **45**, 377; and *ibid.* 1917, **50**, 1123), and with stannic halides, *e.g.* $SnCl_4(NH_2\cdot CHMe\cdot COOH)_4$ (Fichter, Farben-Ztg. 1915, **26**, 274; Chem.-Ztg. 1914, **38**, 693). Fichler and Muller (Arch. Sci. phys. nat. 1916, [iv], **42**, 123; Chem. Soc. Abstr. 1916, i, 766) consider that the weighting of silk by steeping it in a solution of stannic chloride is due to a true chemical combination between the tin salt and the fibroin and its component amino acids, followed by hydrolysis during the washing process. Compounds are formed with neutral metallic salts: $LiCl\cdot(NH_2\cdot CHMe\cdot COOH)\cdot H_2O$; $CaCl_2(NH_2\cdot CHMe\cdot COOH)3H_2O$ (Pfeiffer and Modelski, Z. physiol. Chem. 1912, **85**, 1; Pfeiffer, Ber. 1915, **48**, 1938). The *ethyl ester* has b.p. 48°/11 mm. and sp.gr. 0·9846 at 12·5°; r-*alaninamide*, m.p. 62° (Franchimont and Friedman, Proc. K. Akad. Wetensch. Amsterdam, 1905, **8**, 475); d-*alaninamide* has m.p. 72°

(corr.) and $[\alpha]_D$ +6° in 5·2% aqueous solution ; r-*alanylchloride hydrochloride*,

$$NH_3Cl{\cdot}CHMe{\cdot}COCl,$$

melts and decomposes at 110° ; d-*alanylchloride hydrochloride* has $[\alpha]_D^{20^\circ}$ +7·32° (Fischer, Ber. 1905, **38**, 605, 2914) ; r-*alanineanhydride*, cyclo*alanylalanine* (*dimethyldiketopiperazine*),



has m.p. 282°, and d-*alanineanhydride* has m.p. 297° (corr.) and $[\alpha]_D^{20^\circ}$ −28·8° (Fischer, Ber. 1905, **39**, 453; Maillard, Ann. Chim. Phys. 1915 [ix], **3**, 48). *d*-N-*Methylalanine*,

$$NHMe{\cdot}CHMe{\cdot}COOH,$$

m.p. 165°–166° has $[\alpha]_D^{20^\circ}$ +5·59° ; *l*-N-*methylalanine* $[\alpha]_D^{20^\circ}$ −5·92° ; N-*benzylalanine*, m.p. about 270° (Fischer and Lipschitz, Ber. 1915, **48**, 364 ; *ibid.* 1916, **49**, 1357). *Acetylalanine* $NHAc{\cdot}CHMe{\cdot}CO_2H$ crystallises in rhombic plates *a* : *b* : *c*=0·7792 : 1 : 1·0983 ; m.p. 137° (de Jong, Rec. trav. chim. 1900, **19**, 259 ; Fischer and Otto, Ber. 1903, **36**, 2106) ; *chloracetylalanine ester* $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et$ has m.p. 48·5°–49·5° (corr.) (Fischer and Otto, *l.c.*) ; the *benzenesulphonic derivative*,

$$PhSO_2{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

has m.p. 126° (Hedin, Ber. 1890, **23**, 3197) ; *benzylsulphonalanine*,

$$C_6H_5CH_2{\cdot}SO_2{\cdot}NH{\cdot}CH(Me)COOH,$$

has m.p. 164°–165° (Johnson, J. Amer. Chem. Soc. 1916, **38**, 2135) ; *β-naphthalenesulphonyl*-dl-*alaninamide* $C_{13}H_{14}O_3N_2S$ melts and decomposes at 220° (Kœnigs and Mylo, Ber. 1908, **41**, 4427) ; the d-*camphorsulphonate* of *alanine* $C_3H_7O_2N,C_{10}H_{15}O{\cdot}SO_3H,H_2O$ has m.p. 105°–110°, $[\alpha]_D^{18^\circ}$ +14·33° (Colombano and Sanna, Atti R. Accad. Lincei, 1913 [v], **22**, ii, 234) ; *ethyl* d-*alanine*-d-*bromocamphorsulphonate*,

$$CO_2Et{\cdot}CHMe{\cdot}NH_2,C_{10}H_{14}OBr{\cdot}SO_3H,H_2O,$$

becomes anhydrous at 105°, and melts at 192°, $[\alpha]_D^{20^\circ}$ +67·54° (Gazzetta, 1914, **44**, 1, 97) ; for *hippurylalanine*,

$$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

m.p. 202°, and derivatives, *see* Curtius and Lambotte, J. pr. Chem. 1904 [ii], **70**, 109 ; *phthalylalanine*,

$$C_6H_4 : (CO)_2 : N{\cdot}CHMe{\cdot}CO_2H,$$

m.p. 164°, and *phthaloylalanine*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,H_2O,$$

m.p. 129° (Andreasch, Monatsh. 1904, **25**, 774) ; *palmityl-a-alanine*,

$$CH_3{\cdot}[CH_2]_{14}{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

m.p. 110°, $[\alpha]_D^{10^\circ}$ −5·98° (Aberhalden and Funk, Z. physiol. Chem. 1910, **65**, 61) ; *diethyl dialaninoquinone* $C_6H_2O_2(NH{\cdot}CHMe{\cdot}CO_2Et)_2$ forms red prisms, m.p. 140° (corr.) (Fischer and Schrader, Ber. 1910, **43**, 525) ; 2 : 4-*dinitrophenyl*-dl-*alanine*, m.p. 178° (Abderhalden and Blumberg, Z. physiol. Chem. 1910, **65**, 318) ; d-*alanine picrolonate* (Abderhalden and Weil, Z. physiol. Chem. 1912, **78**, 150) ; 2-d-*alanine*-l-*picrolonic acid* has m.p. about 145° (decomp.) ; l-d-*alanine*-l-*picrolonic acid*, m.p. 215°, decomposed at 217°, $[\alpha]_D^{20^\circ}$ +11·08° (Levene and Slyke, J. Biol. Chem. 1912, **12**, 127) ; d-*alanine picrolonate*, m.p. 214° (decomp.), $[\alpha]_D^{20^\circ}$ +12·4° ; dl-*alanine picrolonate*, m.p. 216° (decomp.) ; *benzyldithiocarboxyl*-dl-*alanine*,

$$CO_2H{\cdot}CHMe{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph,$$

m.p. 136° (Siegfried and Weidenhaupt, Z. physiol. Chem. 1910, **70**, 152). For *dimethyl-a-alanineoxalylglycine*,

$$MeO_2C{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Me,$$

m.p. 98·5°, and other derivatives, *see* Meyeringh (Rec. trav. chim. 1913, **32**, 140).

Among the polypeptides prepared by Fischer, Abderhalden and others, there are many containing the " alanyl " group one or more times, *e.g.* r-*alanylalanine*,

$$NH_2{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

m.p. 276° (corr.), the *benzoyl derivative*, m.p. 203°–204°, the *ethyl ester*, m.p. 114°–116° ; *dialanylalanine*,

$$NH[CHMe{\cdot}CO{\cdot}NH]_2CHMe{\cdot}CO_2H,$$

m.p. 219° (corr.) (Fischer and Kautzsch, Ber. 1905, **38**, 2375) ; d-*alanyl*-d-*alanine*, m.p. 298° (decomp.) $[\alpha]_D^{20}$ −21·6°, Fischer (Ber. 1906, **39**, 453) ; l-*alanyl*-d-*alanine*, m.p. 269°–270° (corr.), $[\alpha]_D^{20^\circ}$ −68·5° ; d-*alanyl*-l-*alanine*, m.p. 275°–276° (corr.), $[\alpha]_D^{20^\circ}$ +68·94° (Fischer and Raske, Ber. 1906, **39**, 2893, 3981) ; l-*ananyl*-l-*alanine*, m.p. 297° (decomp.), $[\alpha]_D^{20^\circ}$ −21·6°, Abderhalden and Gohdes (A. 1932, 194) ; *alanyl glucosamine anhydride* $C_9H_{10}O_5N_2$ turns brown at 245°–250°, and melts at 270° 272° (Weizmann and Hopwood, Proc. Roy. Soc. 1913, A, **88**, 455) ; *ethyl alanylmethylenemalonate*,

$$CO_2Et{\cdot}CHMe{\cdot}NH{\cdot}CH{:}C(CO_2Et)_2,$$

m.p. 206°–207° (Levy, J.C.S. 1914, **105**, 29) ; *alanyl*-p-*hydroxyphenylethylamine* $C_{11}H_{16}N_2O_2$, m.p. 116° (Guggenheim, Biochem. Z. 1913, **51**, 369) ; d-*alanyl*-d-*aminobutyrylglycine*, m.p. 214° (corr.), $[\alpha]_D^{20^\circ}$ +13·86 (Abderhalden, Z. physiol. Chem. 1912, **77**, 371) ; d-*alanylglycyl*-l-*leucine*, m.p. 243°, $[\alpha]_D^{20^\circ}$ −11·2° (Abderhalden and Fodor, *ibid.* 1912, **81**, 21) ; and the tetrapeptide *glycyltyrosyl-glycyl*-d-*alanine* decomposing at 225° (corr.) is probably a mixture of stereoisomerides of the tetrapeptide isolated from silk fibroin (Fischer, Ber. 1908, **41**, 2860 ; *cf.* Abderhalden and Hirszowski, Ber. 1908, **41**, 2840). For other polypeptides derived from alanine, *see* Fischer (Ber. 1904, **37**, 2486, 4585 ; 1905, **38**, 2375, 2914 ; Annalen, 1905, **340**, 128, 152 ; Ber. 1906, **39**, 453 ; 1907, **40**, 943, 1754, 3717 ; Annalen, 1908, **363**, 136), and Abderhalden (Ber. 1908, **41**, 2840, 2857 ; 1909, **42**, 3394 ; Z. physiol. Chem. 1909, **63**, 401 ; 1910, **65**, 417 ; 1912, **77**, 471 ; 1912, **81**, 21 ; Biochem. Z. 1913, **51**, 369).

A micro-method for the estimation of alanine depends upon its conversion to lactic acid and determination as acetaldehyde (Fürth, Scholl, and Herrman, Biochem. Z. 1932, **251**, 404).

β-Alanine, *β-aminopropionic acid*,

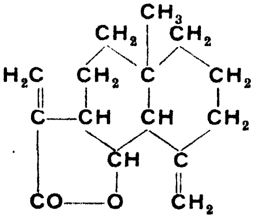
$$H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

prepared by treating β-iodopropionic acid with ammonia (Mulder, Ber. 1876, **9**, 1902 ; Abderhalden and Fodor, Z. physiol. Chem. 1913, **85**, 114), or with silver nitrite and reducing the resulting *nitro*- compound with tin and hydrochloric acid (Lewkowitsch, J. pr. Chem. 1879, [2], **20**, 159) ; by heating ethyl acrylate with alcoholic ammonia in sealed tubes at 110° (Wender, Gazzetta, 1889, **19**, 437) ; or by the action of potassium hypobromite on an alkaline solution of succinimide—this is the best method, and gives a yield of 60% of the theoretical (Hoogewerf and van Dorp, Rec. trav. chim. 1891, **10**, 4 ; Holm, Arch. Pharm. 1904, **242**, 590). Another synthesis is given by Curtius and Hectenberg, J. pr. Chem. 1923, **105**, 289. β-Alanine can be recognised by conversion into ethyl acrylate (Abderhalden and Fodor, Z. physiol. Chem. 1913, **85**, 117).

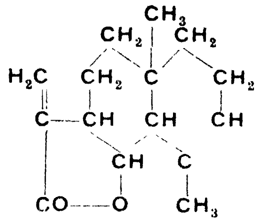
β-Alanine forms prisms, m.p. 196° (Hoogewerf and van Dorp, *l.c.*), m.p. 206°–207° (Lengfeld and Stieglitz, Amer. Chem. J. 1893, **15**, 504) ; needles, m.p. 200° (Abderhalden and Fodor, *l.c.*) ; the hydrochloride of the *methyl ester* has m.p. 94°–95° and of the *ethyl ester* m.p. 65·5°. The *copper salt* $Cu(C_3H_6NO_2)_2,6H_2O$ has the properties of an ordinary copper salt, and not those of a cuprammonium derivative (Callegari, Gazzetta, 1906, **36**, ii, 63).

Free β-alanine does not occur naturally in the body ; when administered with food it causes an increase in the urinary nitrogen, but it is apparently changed with more difficulty than α-alanine, as the increased nitrogen excretion is not observed until the second day (Abderhalden and Schittenhelm, Z. physiol. Chem. 1907, **51**, 323). M. A. W. and W. V. T.

ALANT ROOT. The root of *Inula helenium* (elecampane) contains a bitter principle, related to santonin, which is said to be efficacious against tuberculosis bacilli. The earlier workers (Kallen, Ber. 1876, **9**, 154 ; Marpmann, J.S.C.I. 1887, **6**, 520 ; Brecht and Posth, Annalen, 1895, **285**, 356 ; Brecht and Kallen, *ibid.* 1896, **293**, 352) isolated a number of constituents, of which *helenin* or *alantolactone* and its isomeride iso-*alantolactone* have attracted much attention in recent years. The work of Hansen (Ber. 1931, **64** [B], 67, 943, 1904 ; J. pr. Chem. 1933 [ii], **136**, 176) and of Ruzicka and his co-workers (Helv. Chim. Acta, 1931, **14**, 1090, 1171 ; 1933, **16**, 268) indicates the appended structures, although there is some doubt as to the exact location of the double bonds.



iso-Alantolactone.



Alantolactone.

iso Alantolactone yields on hydrolysis iso-*alantolic acid*, $HO{\cdot}C_{14}H_{20}{\cdot}CO_2H$; this forms a crystalline *ethyl ester*, an *amide*, m.p. 237°–239°, and its *acetyl* derivative, m.p. 212° (Sprinz, Ber. 1901, **34**, 775).

ALBAN. *Albane.* A resin, m.p. 140°, soluble in hot alcohol, contained in gutta percha and balata.

ALBARGIN. Silver-gelatose, a local antiseptic. Some binary metal-gelatoses containing about 5% of silver and 5% of the other metal (zinc, copper, cadmium, mercury, nickel) have greater therapeutic powers than the simple metal gelatoses (G.P. 423080).

ALBASPIDIN, $C_{25}H_{32}O_8$, m.p. 148°, contained in *Filix mas*, *q.v.*

ALBERTITE. The name given to a group of asphaltic pyrobitumens similar to the material which was at one time mined at Hillsborough, Albert County, New Brunswick. It also occurs in Nova Scotia, Utah, and Hanover. It is a jet black solid which is infusible and only partly soluble in carbon disulphide. D. M. W.

ALBERTOLS. Trade name for oil-soluble products obtained by fusing rosin or other natural gum or coumarone resin with a phenol-formaldehyde resin. *Cf.* J.S.C.I. 1912, **31**, 886 ; 1915, **34**, 724, 805 ; Chem.-Ztg. 1922, **68**, 513 ; Ann. Rept. Soc. Chem. Ind. 1922, **7**, 294 ; Kunststoffe, 1922, **12**, 121.

ALBITE. The soda-felspar $NaAlSi_3O_8$.

ALBOCARBON. Trade name for naphthalene.

ALBSAPOGENIN *v.* GYPSOGENIN.

ALBUM GRÆCUM. A term formerly used for the excrement of dogs. It has been used for tanning, as skins treated with it after the removal of the hair and previous to tanning, preserve their softness. It consists mainly of calcium phosphate. Fowls' dung is said by tanners to answer the purpose better.

ALCLAD *v.* ALUMINIUM, AND ALLOYS, LIGHT.

ALCOHOL. The term popularly applied to ethyl alcohol ($CH_3{\cdot}CH_2{\cdot}OH$), the active principle of ordinary intoxicating liquors. Although it has been widely stated that alcohol was known first to the Arabs, this is extremely doubtful and, in all probability, Italy must be credited with its discovery about the ninth century. Ethyl esters occur in many plants and various lichens and from these ethyl alcohol can be obtained by hydrolysis and subsequent distillation.

Preparation.—Ethyl alcohol can be prepared synthetically from its elements by passing an electric arc between carbon poles in an atmosphere of hydrogen. Acetylene (C_2H_2) is produced which, in the presence of nascent hydrogen, is transformed into ethylene (C_2H_4); protracted shaking of ethylene with sulphuric acid yields ethyl sulphuric acid, $C_2H_5 \cdot HSO_4$ (sulphovinic acid), which, on being distilled in the presence of water, produces ethyl alcohol.

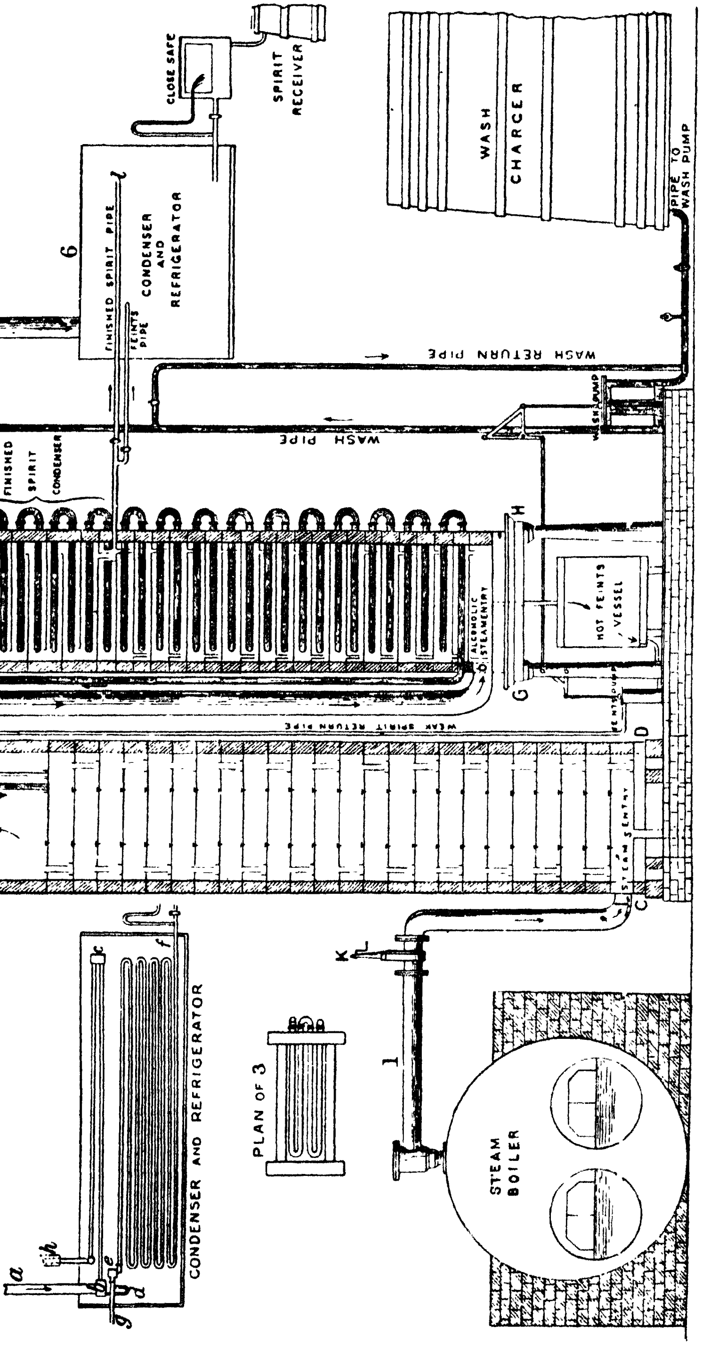
Alcohol is usually prepared by dehydrating the products of the distillation of fermented liquors. Towards the end of the eighteenth century the strongest spirit known contained at least 5% of water. Lowitz (Crell's Ann. 1796, **1**, 1) appears to have been the first to prepare it in an approximately anhydrous condition. He first removed some of the water by adding solid potassium carbonate and, after allowing it to stand for some time, decanted off the spirit. He then added a further quantity of dry potassium carbonate and distilled off very slowly. Richter (*ibid.* 1797, **2**, 211) used calcium chloride instead of potassium carbonate. Drinkwater (Phil. Mag. Feb. 1, 1848), when determining the exact composition of Proof Spirit, first digested ordinary strong spirit with dry potassium carbonate for twenty-four hours, decanted the spirit and further digested it with as much burnt quicklime as was necessary to absorb the whole of the alcohol. He afterwards distilled in a water bath at a temperature of 82·2°, obtaining spirit which had $d^{15\cdot6}$ 0·7946. Further digestion with dry pulverised quicklime for a week at 15·6° and subsequent slow distillation yielded a spirit having *d* 0·7944. Yet a further digestion with hot quicklime at a temperature of 54·4° and distillation out of contact with air at a temperature of 81·1° to 82·2° yielded a product which Drinkwater assumed to be absolute alcohol. It had $d_{15\cdot6}^{15\cdot6}$ 0·793811. According to the latest data this contains 99·95% of absolute alcohol. By following the process of Drinkwater, but distilling in a partial vacuum of 380 to 630 mm., Squibb (Pharm. J. 1886 [iii], **16**, 147) claimed a spirit of $d^{15\cdot6}$ 0·79350. Fownes (Phil. Trans. 1847, 249) was in practical agreement with Drinkwater and, in 1865, Mendeléeff (Pogg. 1869, **138**, 103, 230), when carrying out an investigation for the Russian government, confirmed Drinkwater's finding.

Alcohol may be dehydrated with shavings of metallic calcium, which should be free from calcium nitride and which have been washed with dry carbon tetrachloride to remove traces of petroleum. Twenty grm. of the calcium is used for every litre of strong alcohol. Traces of ammonia which may be present in the distillate can be removed by distilling in presence of tartaric acid. Alizarin (a few centigrams per litre) is dissolved in the alcohol, and a solution of tartaric acid (0·5 g. to 10 ml. alcohol) slowly added until the reddish-blue colour changes to yellow, when the whole is again distilled.

Manufacture.—In its most simple form the early stages in the manufacture of commercial alcoholic spirit are similar to those in the process of brewing beer. In each case endeavour is made to obtain from the original materials the greatest amount of fermentable matter. Whilst, however, the brewer strictly controls his process in order to obtain a final product of a required gravity and thus restricts the production of alcohol, the spirit manufacturer aims at a maximum alcoholic yield. To obtain this he produces a wort containing more maltose and less dextrinous matter than that of the brewer and having a specific gravity not more than 1,040 when set for fermentation. To prevent the formation of a large amount of fusel oil, fermentation should be started at a temperature of not more than 25°. In order to avoid the growth of acetic and other ferments, which would involve a reduction in the yield of ethyl alcohol, the yeast should be as pure as possible. In modern distilleries where spirit for industrial purposes is manufactured it is customary to employ pure cultures grown from a single yeast cell.

Until the early years of the present century the methods employed in Great Britain for the production of alcohol could be regarded as the direct developments of the old-established preparation of whisky and other potable spirits. The materials used consisted chiefly of malt, maize, rice, sago, tapioca, barley, rye, oats and other farinaceous products. Molasses, from which large quantities of alcohol are now derived, was used only to a limited extent. The smaller distillers use malt principally and the spirits produced are sold under various geographical and proprietary names. In such cases the process of manufacture consists in distilling the fermented wort—known as wash—in a common still, collecting the distillate, which is called "low wines" and is weak spirit contaminated with fusel oil, and redistilling. The spirit which passes over in the redistillation is that which is used for consumption. It contains from 60 to 75% of alcohol by weight (approximately 20 overproof to 45 overproof), but before being sent into consumption or placed in bond it is diluted down to a strength of about 30 overproof. The materials used in the manufacture of Irish whisky are usually a mixture of malt and grain. It is generally bonded at a strength of about 25 overproof (64% of alcohol by weight).

Until the present century the demand for alcohol of a greater strength than that produced by these methods was so limited that the general adaptation of the manufacturing processes to produce a stronger spirit was not justified and the comparatively small quantity required was obtained by subsequent dehydration. The great development in the commercial production of alcohol was associated with the introduction of the Coffey still, which, with various modifications and developments, still forms the basis of the elaborate apparatus used for large-scale production of alcohol at the present time. A Coffey still of simple form is shown in the annexed illustration. The left-hand column is called the *analyser* and the right-hand one the *rectifier*. The first operation is to fill both columns with steam. This is accomplished by introducing it under pressure from the boiler at C, whence it ascends within the analyser, passing by the pipe M into the bottom of the rectifier. When a proper temperature has been attained the wash is pumped from the wash charger by a pipe which enters the top of the rectifier. This pipe is only shown


ALCOHOLIC STEAM EXIT
WASH ENTRY
FINISHED SPIRIT CONDENSER
FINISHED SPIRIT PIPE
FEINTS PIPE
6
CONDENSER AND REFRIGERATOR
l
CLOSE SAFE
SPIRIT RECEIVER
WASH CHARGER
PIPE TO WASH PUMP
WASH RETURN PIPE
WASH PIPE
WASH PUMP
H
HOT FEINTS VESSEL
G
FEINTS PUMP
ALCOHOLIC STEAM ENTRY
WEAK SPIRIT RETURN PIPE
D
E
3
F
M
WASH EXIT
WASH ENTRY
B
STEAM EXIT
2
A
STEAM ENTRY
C
K
1
STEAM BOILER
PLAN OF 3
CONDENSER AND REFRIGERATOR
a
b
c
d
e
f
g
h

sectionally in the sketch after entering the column, but it is continuous, and the wash passes slowly through it, becoming warmer, owing to the pipe being in contact with the steam. When it has reached the bottom of the rectifier it is not far from the boiling-point. It will be seen that the pipe then ascends and finally delivers the wash into the top of the analyser. The lines across the analyser represent plates of perforated copper and in connection with each is a tube which projects about an inch and a half above the plate and dips into a shallow vessel placed on that next beneath. The wash, on entering, falls on the first plate but on reaching a depth of an inch and a half passes through the tube to the second one. In the meantime the steam produces ebullition in the wash liquor lying on the plates and carries away with it the alcoholic vapour through the steam exit pipe, so that by the time the wash has reached the bottom of the column it has been deprived of its alcohol. The alcoholic vapour passes by the pipe M into the bottom of the rectifier which, like the analyser, contains plates and metal tubes, and where a process of gradual cooling takes place by the action of the pipe carrying the cold wash. Fusel oil vapour, condensing at a higher temperature than alcohol, is the first to assume liquid form and, contaminated with spirit, passes into the hot feints receiver. The vapour containing alcohol continues to ascend, meeting with portions that have condensed and are undergoing the process of rectification. It will be seen that the upper part of the apparatus is marked off in the sketch as "finished-spirit condenser." It is so called because all that condenses within its area, instead of returning towards the bottom of the apparatus to be rectified, passes by the finished-spirit pipe or feints pipe into the receivers. At the top of the apparatus is a pipe marked "alcoholic steam exit," which carries away most of the aldehyde as well as any spirit vapour which, under special circumstances, may not have been condensed before reaching that point.

Various modifications of this still have been made to meet special requirements such as the production of a spirit of greater purity and the elimination and recovery of fusel oil as a by-product. The spirit produced in these "patent stills," so called to distinguish them from the old "pot" stills, has been used only to a limited extent for the production of spirit for whisky blending. Larger quantities are transferred to the rectifiers, who redistil them with flavouring ingredients producing gin, British brandy, British rum and the various cordials. The great bulk goes into industry for use as a raw material or as a technical solvent and as for many of these purposes it is essential that the alcohol should be anhydrous, it is to meet the greatly increased demand in this connection that the most important development in the methods of production has taken place. The new demand has been associated more particularly with the lacquer, varnish and film industries, whilst the advantage derived by its addition to mineral oils, in order to obtain fuel for internal combustion engines, justifies the anticipation of an increased demand in the future. In view of the great commercial possibilities indicated, the direct production of absolute alcohol on a large scale, involving but one distillation, is of the utmost importance.

The azeotropic method is one which has been considerably developed and completely meets this demand. The highest strength alcohol which can be obtained by fractional distillation is that containing 95% of alcohol by weight. At this concentration the spirit boils constantly at a temperature of 78·15° as if it were a pure substance. Similarly anhydrous ethyl alcohol forms with benzene a mixture having a constant boiling-point of 68·25° and, if water is present, a ternary azeotropic mixture is formed which boils at 64·85°. Thus, if benzene be added to alcohol containing a little water and the mixture is distilled, the ternary azeotropic mixture distils off first followed, if further benzene is present, by a fraction of the binary mixture, leaving behind the excess alcohol in an anhydrous state and boiling at 78·35°. Observation of this phenomenon by Sidney Young of Dublin University (Young and Fortey, J.C.S. 1902, **81**, 739) led to the issue of a patent for its commercial development in 1903. Whilst, by this method, absolute alcohol can be produced from (*a*) rectified alcohol, (*b*) the impure aqueous distillate, or (*c*) the fermented wort, the last involves the lowest steam consumption and the highest yield (R. Jumentier, Bull. Assoc. Chim. Sucr. 1931, **48**, 396). The Usines de Melle (Distilleries des Deux-Sèvres) and other Continental distilleries have reduced the three stages, distillation of the mash, rectification of the raw spirit and dehydration of the rectified spirit, into one process by this means. This has resulted in greater expedition in production, increased convenience in working, economy in the space required and reduction of the consumption of steam compared with the amount of absolute alcohol produced. With regard to alternative dehydrating liquids, "benzine" (100°–101°) and benzene are both recommended, and each possesses certain advantages over the other. Thus "benzine" separates more water than benzene and gives an easier separation but, on the other hand, it takes out more of the alcohol. In order to obtain the best results a mixture of the two is frequently used. The small traces of the dehydrating substances which may be left in the final product and which may render it unsuitable for certain purposes, can, according to the Reichsmonopolverwaltung für Branntwein, be removed by filtering through active charcoal (D.R.P. 529-381, Fritzweiler and Dietrich, Z. Spiritusind. 1930, **53**, 27).

A further method described by Fritzweiler and Dietrich (Angew. Chem. 1932, **45**, 605) involves the use of trichloethylene as an entraining agent. By this process anhydrous ethyl alcohol, free from even the traces of methyl alcohol which may be present, and which is collected separately, can be obtained simultaneously with the use of only three columns, whilst the method can be adapted for the production of absolute alcohol direct from fermentation liquors.

The development of the original methods of Drinkwater and other early workers for the dehydration of alcohol by means of salts *e.g.* potassium carbonate, or freshly burnt quicklime, has often been attempted but has been found to be impracticable on a commercial scale. The Hiag-Holzverkohlungs-Industrie G.m.b.H., Konstanz have, however, overcome the difficulties and produced a method of continuous dehydration by means of potassium and sodium acetates in aqueous solution. It is claimed for the process that the steam consumption is lower than in any other, whilst the loss of alcohol is small. Dehydration by means of calcium sulphate has been developed by the I.G. Farbenindustrie A.-G. It is of interest to note that all these methods produce alcohol of remarkable purity, whilst the mineral salts used are readily recovered for further use in a subsequent operation.

Coincident with the alteration and development of the method of manufacture of alcohol, the raw material used for its production has undergone considerable change.[1] Molasses has now largely replaced farinaceous substances, not only in Britain but also in America, where it is estimated that not more than 10% of the total output is obtained from materials other than molasses. In the method described by S. D. Labayen (Sugar News, 1931, **12**, 632) the molasses is diluted to a specific gravity of 1·06 to 1·075, acidified with sulphuric acid to prevent the growth of undesirable yeasts, and seeded with a pure yeast culture. Ammonium sulphate is sometimes added as a yeast food, to hasten alcoholic fermentation and thus inhibit, as far as possible, the growth of wild yeasts. Fermentation is complete in 48–60 hours, the temperature gradually rising to 35°–37°. The final alcoholic content is 5·5 to 7%.

Attempts have also been made, especially in America, to produce alcohol from wood by the Classen process or some modification of it. The cellulose of the wood is converted into dextrose and other sugars by treatment with dilute acid under pressure. The sugary mass is then fermented with yeast and distilled. The yield is about 21 gallons of 95% alcohol per ton of wood. The waste liquors from the manufacture of wood pulp by the sulphite process have also been used. The liquors contain from 1 to 2% of sugars which, after neutralisation or removal of the sulphur dioxide, can be fermented and the alcohol recovered by fermentation. The method is used in Northern Europe and in North America with some success, although the spirit obtained is not of high purity.

The synthetic production of alcohol from acetylene, produced from calcium carbide, was largely developed in Germany during the war. The methods employed consist either in transforming the acetylene into ethylene and thence into alcohol by treatment with oil of vitriol and water, or by converting the acetylene into aldehyde in the presence of a catalyst, such as a mercury salt, and then reducing the aldehyde to alcohol by passing its vapour, mixed with hydrogen, over finely divided nickel at a particular temperature. The method is also used in America, some three to four million gallons of alcohol being thus produced annually.

Alcoholic Standards.—The British Standard Specification (No. 507—1933) for ethyl alcohol includes a provision that it "shall be clear, colourless, and free from matter in suspension and shall contain no adulterants of any kind" and provides that it shall be 66° overproof, but may fall within the range of 61° to 68° overproof if agreed between purchaser and vendor. The British Pharmacopœia of 1932 prescribes absolute alcohol as containing not less than 99·4% by volume or 99% by weight of pure alcohol, whilst the limits for "alcohol" are defined as not more than 95·2% by volume or 92·7% by weight and not less than 94·7% by volume or 92% by weight. Various "official" dilute alcohols are recognised by the same authority for use in pharmacopœial preparations, No. 1 in the following table being known as "rectified spirit."

No.	Per cent.	Mls. of 95% alcohol diluted to one litre with distilled water.	Specific gravity 15·5°/15·5°	Refractive index at 20°.
1	90	948	0·832–0·835	1·3645–1·3647
2	80	842	0·863–0·865	1·3649–1·3648
3	70	737	0·889–0·891	1·3638–1·3636
4	60	632	0·913–0·914	1·3618–1·3617
5	50	526	0·934–0·935	1·3589–1·3587
6	45	474	0·943–0·944	1·3572–1·3570
7	25	263	0·9705–0·9713	1·3473–1·3467
8	20	210	0·9755–0·9765	1·3442–1·3436

According to the Pharmacopœia of the United States of America dehydrated or absolute alcohol contains not less than 99% by weight of $C_2H_5{\cdot}OH$, "alcohol" contains not less than 92·3% by weight of $C_2H_5{\cdot}OH$, and "diluted alcohol" contains not less than 41% and not more than 42% by weight of $C_2H_5{\cdot}OH$.

Properties.—Anhydrous ethyl alcohol is a colourless liquid having a specific gravity of 0·791 at 20°/20° (Lowitz, Crell's Ann. 1796, **1**, 1), 0·7938 at 15·6°/15·6° (Fownes, Phil. Trans. 1847, 249), 0·793811 at 15·6°/15·6° (Drinkwater, Phil. Mag., Feb. 1, 1848), 0·79350 at 15·6°/15·6°, 0·79367 at 15°/4° (Mendeléeff, Pogg. 1869, **138**, 230; Squibb, Ephemeris, 1884–5, and Pharm. J. 1886 [iii], **16**, 147), 0·7851 at 25°/4° (Winkler, Kailan, Osborne, McKelvy and Bearce, J. Washington Acad. Sci. 1912, **2**, 95), 0·7936 at 15°/4° (Schoorl and Regenbogen, Proc. K. Akad. Wetensch. Amsterdam, 1918, **20**, 831), 0·80628 at 0°/4° (Young, J.C.S. 1902, **81**, 717; Klason and Norlin, Arkiv Kemi., Min., Geol. 1906, **2**, No. **24**,

---

[1] During the year ended September 30th, 1936, the materials used in producing just over sixty million proof gallons in the seventy-six distilleries in Great Britain and Northern Ireland were: malt 1,398,277 cwt., unmalted grain 1,835,417 cwt., and molasses 6,168,402 cwt.

1 ; Merriman, Trans. Chem. Soc. 1913, **103**, 630). The boiling-point at 760 mm. has been redetermined by W. Swietoslawski and others (Compt. rend. 1932, **194**, 357) on three separate samples dehydrated by different methods, viz. distillation, azeotropic distillation with benzene, and azeotropic distillation with carbon disulphide. The distillations were carried out with a Swietoslawski rectification column in an atmosphere of nitrogen. The boiling-points of the three samples were 78·320°, 78·318°, and 78·319° respectively. Wroblewski and Olsewski (Compt. rend. 1883, **96**, 1140 and 1125) found that ethyl alcohol solidified at −130·5°, but the temperature given by Ladenburg and Krügel (Ber. 1899, **32**, 1818) was −112·3°. Ethyl alcohol has a specific heat of 0·6120 at temperatures between 16° and 40·5° (Schüller, P. Erg. **5**, 116–192). Its index of refraction for $H\beta$ = 1·3667 (Brühl) and its critical temperature 243·6° at 48·9 m. At this point 1 grm. occupies 3·5 c.c. (Ramsay and Young, Proc. Roy. Soc. 1885, **38**, 329).

Vapour pressure of ethyl alcohol (Merriman, Trans. Chem. Soc. 1913, **103**, 632) :

Temperature °C.	Pressure in mm.	Temperature °C.	Pressure in mm.
0	12·0	18	38·7
1	12·9	19	41·2
2	13·9	20	43·8
3	14·9	21	46·5
4	15·9	22	49·4
5	17·0	23	52·4
6	18·2	24	55·6
7	19·4	25	59·0
8	20·7	30	78·6
9	22·1	40	134·9
10	23·5	50	222·2
11	25·1	60	352·7
12	26·7	70	542·5
13	28·4	80	812·7
14	30·3	90	1,187·0
15	32·2	100	1,694·0
16	34·3	105	2,007·0
17	36·4		

The viscosity of ethyl alcohol at various temperatures has been determined by Thorpe and Rodger (Phil. Trans. 1894, **185**, II, 533) with the following results :

Temperature °C.	η	Temperature °C.	η
7·16	0·015328	42·84	0·007875
13·23	0·013573	49·37	0·007047
19·22	0·012094	55·57	0·006354
25·24	0·010792	61·07	0·005815
31·89	0·009560	67·55	0·005253
37·51	0·008644	73·57	0·004764

The dielectric constants of various mixtures of alcohol and water, at temperatures ranging from −5° to 40°, have been determined by J. Wyman, Jun. (J. Amer. Chem. Soc. 1931, **53**, 3292), whilst by use of a resonance method at a wave-length of 150 m. determinations were also made by Åkerlöf (*ibid.* 1932, **54**, 4125).

Ethyl alcohol is hygroscopic and is miscible with water in all proportions. On adding water to anhydrous alcohol a considerable development of heat occurs, owing to the contraction in the resultant volume of the mixture as compared with the sum of the volumes of the separate liquids. The point of maximum contraction is approximately at the mixture of 48 volumes of water with 52 volumes of anhydrous alcohol. H. T. Brown (Analyst, 1915, **40**, 379) suggests that in the mixtures of very dilute alcohol and water there is a slight expansion instead of contraction, his suggestion being based upon data obtained from the British official alcoholometric tables compiled by Thorpe and others. Dietrich and Lohrengel (Z. Spiritusind. 1933, **56**, 232) have determined the air content of aqueous alcoholic mixtures. They find that water contains 18·9 and alcohol 145·7 ml. of air per litre at 20°, whilst the oxygen content of the contained air varies from 34% in water to 29% in alcohol. Ethyl alcohol is inflammable, the combustion evolving great heat but little light and producing carbon dioxide and water. F. D. Rossini (Bur. Stand. J. Res. 1932, **8**, 119) estimates the heat of combustion of ethyl alcohol in the liquid state at 25° and a constant pressure of one atmosphere to be 1366·31±0·40 international kilojoules or 326·61±0·10 kg.-cal. per molecule. Strong alcohol acts as a caustic irritant in contact with the tissues of the body, owing probably to the energy with which it withdraws moisture from the surface. In addition to physical tests (*see* ALCOHOLOMETRY) the British Pharmacopœia prescribes certain simple tests for the purity of ethyl alcohol including the following : 20 ml. does not require more than 0·2 ml. of *N*/10 sodium hydroxide to give a pink colour with phenolphthalein (test of acidity) or more than 0·1 ml. of *N*/10 sulphuric acid to give a red colour with methyl red (test of alkalinity). Oily or resinous substances are indicated if, on the addition of water in any proportion, the solution does not remain clear. As a test for fusel oil and allied impurities, on evaporating 25 ml. almost completely, no foreign odour should be perceptible and the addition of one ml. of sulphuric acid should not produce a red or brown colour. Aldehyde above the limit is indicated if, after mixing 10 ml. with 5 ml. of sodium hydroxide solution and allowing the mixture to stand for five minutes, a yellow colour is produced.

Anhydrous alcohol should give no cloudiness when mixed with benzene, no pink coloration when shaken with a crystal of potassium permanganate and no turbidity or evolution of gas (acetylene) in contact with calcium carbide. Anhydrous alcohol added to a fragment of anthraquinone and sodium amalgam acquires a green colour but if a trace of water be present the colour becomes red (Claus, Ber. 1877, **10**, 927).

Detection and Estimation.—In view of the extended use of mixed solvents in commerce the detection and estimation of ethyl alcohol has become increasingly difficult and important. Many methods have been devised to meet special conditions, the following qualitative methods being in most general use. (For methods of estimation, *see* ALCOHOLOMETRY.)

"*Resin*" *Test.*—An aliquot part of the purified distillate (usually 10–30 ml.) is placed in a small flask and diluted to 50 ml. with water. Ten drops of concentrated sulphuric acid and about 5 grm. of potassium bichromate are added. A bent tube is attached, the free end dipping into a tube containing about 2 ml. "Kjeldahl soda" (30% solution). The contents of the flask are very slowly raised to boiling, and so continued until the soda is also in a state of ebullition. The presence of ethyl alcohol in the original sample is indicated by the production of a bright yellow resin (aldehyde resin) having a characteristic odour. When the proportion of alcohol is very low—say 0·1% or less—the characteristic odour is produced even when only slight opalescence is visible. Higher alcohols yield a white opalescence or a yellow resin possessing a different odour (J. C. Thresh, Pharm. J. 1878 [ii.], ix, 408).

"*Dimedon*" *Test.*—This is based upon the conversion of ethyl alcohol to acetaldehyde and the condensation of the aldehyde with "dimedon," *i.e.* dimethyl-dihydro-resorcinol (Vorländer, Z. anal. Chem. 1929, **17**, 241). The alcoholic solution is oxidised by boiling with a saturated solution of potassium bichromate in 15% sulphuric acid. It is then distilled into an ice-cold 0·2% solution of "dimedon" in water. On allowing to stand for some hours the condensation product is precipitated. It is filtered off, dried and the melting-point determined. If derived from ethyl alcohol this is 141·5°, compared with methyl alcohol 187°, propyl alcohol 148·5°, and butyl 132° (doubtful). There is no precipitate from *iso*propyl alcohol.

Refractometer Test.—The specific gravity and reading on the immersion refractometer are ascertained and the percentage of alcohol determined by reference to appropriate tables (*see* ALCOHOLOMETRY). If only ethyl alcohol be present the two determinations will agree.

Ethyl alcohol is readily detected by the formation of ethyl acetate on adding sodium acetate and a few drops of acetic acid to the liquid to be tested, together with an equal volume of strong sulphuric acid, and heating the mixture, when the characteristic smell of ethyl acetate is produced. A less characteristic reaction is the formation of iodoform when the liquid is mixed with a few drops of a solution of iodine and warmed and the colour of the iodine destroyed by a solution of sodium carbonate or hydroxide. I. M. Korenman (Z. anal. Chem. 1933, **93**, 335–43) suggests that the test is improved by using potassium hydroxide at a temperature of 50°. If the liquid to be tested is rendered alkaline and shaken with benzoyl chloride, until the odour of the chloride has disappeared, ethyl benzoate is formed and recognised by its odour.

According to Pasteur very small traces of ethyl alcohol, especially in fermented liquors, may be detected on distilling the suspected aqueous liquid and observing the formation of striæ or "tears" produced by the condensation of the first few drops of the distillate. A few ml. of the liquid to be tested are placed in a wide test tube fitted with a cork and a long glass tube. The liquid, which should contain a spiral of copper or platinum wire or a few fragments of pumice to ensure regular ebullition, is heated by a small flame and the formation of the "tears" in the long tube noticed. With care as little as 0·001% of alcohol can be detected in this way.

Alcohol forms ethoxides with sodium and potassium, and unstable compounds with certain crystalline salts, *e.g.* zinc chloride, the latter called alcoholates. Subjected to the action of a limited supply of oxygen, it is converted into aldehyde (C_2H_4O), which, by further oxidation, becomes acetic acid ($C_2H_4O_2$). Distilled with chloride of lime, it forms chloroform ($CHCl_3$). With sulphuric acid at a temperature not exceeding 145° it yields ether ($C_4H_{10}O$). With twice its bulk of sulphuric acid at a temperature of 170° it gives ethylene (C_2H_4). With excess of dry chlorine gas it produces chloral (C_2HCl_3O). For the detection of ethyl alcohol in acetone, 3 ml. of Agulhon's reagent (0·5 gm. of $K_2Cr_2O_7$ dissolved in 100 ml. of pure nitric acid, density 1·310) added to 1 ml. of acetone gives a blue colour if 0·5% of ethyl alcohol is present (Craven, J.S.C.I. 1933, **52**, 239T).

A method for the determination of *iso*propyl alcohol in ethyl alcohol is suggested by Archibald and Beamer (Ind. Eng. Chem. (Anal. Ed.) 1932, **4**, 18), which appears to be satisfactory if not more than 20% of *iso*propyl alcohol is present. If a larger proportion is present the mixture must be diluted with a known quantity of ethyl alcohol. Ten ml. of the sample are placed in a 50-ml. glass-stoppered graduated cylinder with 20 ml. of 30% sodium hydroxide solution. The temperature is kept below 25° by immersion of the cylinder in a bath. After repeated shaking and subsequent separation 1 ml. of the upper alcoholic layer is drawn off and titrated with 0·1*N*-sulphuric acid using methyl red as an indicator. Reference to the appropriate graph will give the proportion of *iso*propyl alcohol. For the determination of propyl alcohol in ethyl alcohol the sample should be adjusted to an alcoholic strength of 40% and distilled with CrO_3 and H_2SO_4 into a cooled receiver. Three drops of a 2% alcoholic solution of vanillin and 4 ml. of fuming HCl are added to 0·6 ml. of the distillate and the mixture heated to 65° for six minutes and then cooled. The colour of the cool solution varies from orange (if 3% propyl alcohol) to deep purple (20%). The colour can be standardised against known mixtures or a solution of colloidal copper ferrocyanide (Noetzel, Z. Unters. Lebensm. 1932, **64**, 288).

Although it is undeniable that an excessive quantity of ethyl alcohol has a deleterious effect upon the human organism, it is probable that observations on which this opinion is partly based have been vitiated by the presence of impurities such as higher alcohols and furfural. Thus Dugar-din-Beaumetz and Audige found during experiments on dogs that the lethal dose of various alcohols in grms. per kilo body weight was : ethyl 5 to 6, propyl 3·75, butyl 1·8, and *n*-amyl 1·5. The use of inferior or decomposing materials in the original mash is likely to result in the presence in the resultant spirit of volatile bases such as pyridine, which would undoubtedly have a bad effect, similar to alkaloidal poisoning, upon the consumer. According to Widmark (Biochem. Z. 1933, **259**, 285–93) the lethal concentration of alcohol in the blood is 0·5%. For children during the first year of life 11–14 gm. of ethyl alcohol is sufficient to cause death. The maximum alcoholic concentration per day cannot exceed a certain limit, which for a man of 70 kilogrm. corresponds to 170 grm. and for a woman of 60 kilogrm. corresponds to 120 grm., while for a child during its first year it is 12 grm. Dervieux and others (Ann. méd. legale criminal police Sci. 1933, **13**, 458) have found that the minimum rapidly lethal dose of ethyl alcohol is of the order of 10 ml. per kilo body weight, whilst slightly smaller doses (8–9 ml.) may produce death in 20–48 hours. In such cases, or when death does not occur, the ethyl alcohol content of the blood 24 hours after administration may vary within wide limits (0–6·75 ml. per litre), according to the symptoms produced. This is due to the fact that ethyl alcohol is destroyed in the body by oxidation and eliminated through the lungs and kidneys, these phenomena being reduced in the comatose state and accelerated when the alcohol produces excitation. Ariyama (J. Agric. Chem. Soc. Japan, 1933, **9**, 1035) has observed, in experiments on rats, that the nutritive effect of food was increased by the addition of 5% of alcohol. The average percentage of ethyl alcohol in body tissues has been determined by Gettler and others (J. Amer. Chem. Soc. 1932, **54**, 1476) as follows : human brain 0·0004, human liver 0·00256, human blood 0·004, dog brain 0·003, dog liver 0·0007, dog blood 0·0013, and pig brain 0·0007. In dogs moderate intoxication has been found to give an alcoholic content of 0·25% in the blood. Both intoxication and blood-alcohol concentration are lowered when alcohol is ingested with or following food. Goldhahn (Klin. Wochschr. 1932, 1834) found that in every case in which the concentration of alcohol in the blood amounted to 2·7% or more, intoxication could be assumed to be proved. Normally 1·5 hours after taking alcohol the alcoholic concentration of the blood has reached its maximum, then gradually decreasing and becoming normal after 12–15 hours. The rate of destruction of alcohol in the blood is constant after ingestion of strong or weak solutions in animals not accustomed to alcohol, but is increased 60% in accustomed animals (Turner and Loew, Pharmacol. 1932, **44**, 305).

For medico-legal purposes the estimation of alcohol in blood is becoming increasingly important. Nicloux (Comp. rend. Soc. Biol. 1931, 107, 68) suggests a method based upon the oxidation of the alcohol with potassium dichromate and sulphuric acid, the amount of dichromate necessary to change the colour from greenish blue to greenish yellow being an indication of the percentage of alcohol. Mayer (Deut. Z. ges. gericht. Med. 1932, **18**, 638) has modified the method by oxidising the alcohol to acetic acid with potassium dichromate and phosphoric acid, the excess of Cr_2O_7 being titrated with thiosulphate solution. Certain workers, however, prefer the method of Widmark (Biochem. Z. 1922, **131**, 473). This depends upon the distillation of the alcohol from the blood (one drop) into a standard solution of potassium dichromate in concentrated sulphuric acid, with subsequent oxidation with that reagent. Excess reagent is determined by addition of potassium iodide followed by titration of liberated iodine with 0·01 or 0·005*N* sodium thiosulphate, all operations being checked by suitable controls.

Uses.—In addition to forming the basis of many beverages, commercial ethyl alcohol is employed as a solvent for many of the drugs required in medicine and forms part of a large proportion of the tinctures of the materia medica. It is also used largely as a solvent for essential oils and in preparing perfumes and essences, whilst ether and ethyl derivatives are manufactured from it. Its use has been widened by its extensive adoption as a solvent in the varnish and film industries. One of the most important recent developments of the use of alcohol is as the raw material in the manufacture of the acetic acid required in the rayon acetate industry. There are also great possibilities of its ultimate use in internal combustion engines. It is not, however, a practical substitute for petrol or benzol in engines designed for those fuels, it being uneconomical owing to the difficulty of vaporisation and high consumption. Mixtures of alcohol up to 30% with petrol are satisfactory if the alcohol is anhydrous, whilst mixtures of alcohol, benzene and petrol in the proportions of 20 : 30 : 50 or 10 : 40 : 50 make good fuels (Howes, World Petroleum Congress, London, 1933, Proc. 2, 751). On the other hand, Teodoro (Philippine Agr. 1931, **20**, 295) states that, with a slight alteration of the carburettor and ignition, tractor engines designed for petrol can be used with ethyl alcohol, giving smoother running, steadier pull and absence of overheating, knocking, corrosion or deposition of carbon. A mixture of alcohol with an equal quantity of ether is suggested by Amatriain (Rev. ing. ind. Madrid Z. 1931, No. 15, 235) but slight changes in the carburettor being necessary. In Germany, France, Sweden, Hungary, Italy and Latvia laws have been enacted making the use of a definite proportion of ethyl alcohol in motor fuel compulsory, whilst there is prospect of similar legislation in other countries.

Methylated Spirit.—In response to strong representations made to the British Government to permit the use of alcohol duty free for commercial and certain other purposes, regulations were issued in 1855 permitting the use, free of duty, of a mixture of nine parts of spirits of wine and one part of methyl alcohol (wood-naphtha). This could be done only under strict Revenue control, however, the principal restriction being that the methylated spirit, as it was called, could be kept only by authorised persons and in authorised premises. In 1861 the concession was extended to all other purposes except consumption as a beverage or as a medicine. The reasons for selecting wood-naphtha were that, whilst it would be least likely to interfere in any of the commercial processes for which alcohol was required—especially as a solvent—it would be very difficult to separate from the alcohol when once mixed. The precautions taken to prevent the improper use of methylated spirit were found to be ineffective. It was possible to purify it sufficiently to render it potable and it was found that even in its untreated state it was consumed by addicts in increasing quantity. In 1891, therefore, the use of the original methylated spirit was restricted to manufacturers only and then under Revenue control, whilst for general purposes mineralised methylated spirit (denatured also with mineral naphtha) was introduced for sale by licensed retailers to the general public. In 1918 a Departmental Committee investigated "the suitability of alcohol, either alone or in admixture with solid, liquid, or gaseous combustible substances, for use in internal combustion engines" and "the question of denaturing the alcohol." As a result of the recommendations of this committee special provision for "power methylated spirit" was made in the Finance Act of 1920 and the subsequent Power Methylated Spirit Regulations of 1921 (*see* Statutory Rules and Orders, 1921, No. 1318). In 1925 a yet further standard denatured spirit was authorised, an additional denaturant—pyridine—being added to industrial methylated spirit.

Thus at the present time the following methylated spirits are officially recognised in the United Kingdom:

(*a*) *Industrial Methylated Spirit*, which must contain not less than 5% of approved wood-naphtha.

(*b*) *Mineralised Methylated Spirit*, in which to every 90 parts by volume of spirits must be added 9½ parts by volume of wood-naphtha and ½ part of crude pyridine. To every 100 gal. of this mixture must be added ⅜ gal. of mineral naphtha (petroleum oil) and not less than $\frac{1}{40}$ oz. by weight of powdered aniline dye (methyl violet).

(*c*) *Power Methylated Spirit*, in which to every 100 volumes of spirits must be added 2½ volumes of wood-naphtha, ½ volume of crude pyridine, and not less than 5 volumes of petrol or benzol. To this mixture must be added "Spirit Red III" dye in the proportion of 0·25 oz. weight to every 1,000 gal.

(*d*) *Industrial Methylated Spirit* (*Pyridinised*), in which to every 95 volumes of spirits must be added 5 volumes of wood-naphtha and to every 100 volumes of the mixture must be added ½ volume of crude pyridine. This preparation may be used in the manufacture of "finish," which is defined as a mixture of methylated spirit and any gum resin in which the proportion of gum resin in actual solution is not less than 3 oz. to the gallon.

Other Duty-Free Spirit.—When it is proved to the satisfaction of the Commissioners of Customs and Excise that methylated spirit, if used in any particular manufacturing or other process, would be detrimental or unsuitable, the Commissioners may, under powers conferred upon them by the Finance Act of 1902, allow the use of duty-free spirit not methylated. This concession is subject to strict Revenue control and is more readily granted when the substances added in the course of manufacture may be regarded as denaturants replacing the wood-naphtha present in methylated spirit. For purposes of research, however, the Commissioners have power to allow the use of ethyl alcohol duty free, but the more lightly denatured spirits are allowed to be used only under increasingly stringent control.

Dominions and Colonies.—Throughout the British Empire the regulations governing the use of methylated spirit approximate closely to those in force in Great Britain. In Australia the generally recognised denaturants are wood-naphtha, benzene, benzine, pyridine and crystal violet in varying proportions for different purposes. In South Africa the standard formula is spirits 95·0 gal., crude methyl alcohol 3·5 gal., and pyridine bases 1·5 gal. This formula may, subject to the approval of the Commissioner of Excise, be varied in special circumstances, and Simonsen oil with pyridine is often the denaturant. In Canada there are seven grades of "specially denatured alcohol" and three grades of "denatured alcohol," the alternative denaturants being wood-alcohol, benzine, benzene, iodine, potassium iodide, diethylphthalate, brucine sulphate, ethyl acetate, toluol, nitrobenzol, pine oil and pyridine. In India spirit is usually denatured with 0·5% light caoutchoucine and 0·5% of pyridine bases of mineral origin. In other parts of the Empire, in addition to the more common denaturants, kerosene, turpentine, shellac and other substances are used.

Other Countries.—The introduction of alcohol denaturation by Great Britain in 1855 has been followed by similar measures in nearly all foreign countries, the details varying to suit local requirements. In the United States of America there are, for general use, alternative formulæ, the principal denaturants being wood-alcohol, benzine, benzene, nitrobenzol, pyridine, pine oil and aniline oil. For motor power 5 gal. of sulphuric ether, 2 gal. of benzine, and 1 gal. of pyridine or aniline oil are added to 100 gal. of ethyl alcohol. There are also special formulæ for approved specific purposes. In Germany the principal denaturants are wood-spirit, pyridine, turpentine, toluene and benzine. For power purposes wood-spirit, pyridine, methyl violet and benzol are added to the alcohol. Special denaturants are allowed for specific purposes. In France the denaturant for general purposes is "methylene type regie." This must indicate at least 90% alcohol, and contain 25% acetone and at least 2·5% pyrogenous impurities produced by wood distillation. Five and a half litres of the denaturant must be added to 100 litres of spirit, which must not contain more than 1% of essential oils and must indicate at least 90% alcohol.

In order that the wood-naphtha which is used as a denaturant shall be effective it is essential that it shall be so nauseous that the spirits in which it is mixed are incapable of being added to potable spirits without rendering them unfit for human consumption. For the information of traders the British authorities have issued information relating to the tests to which the naphtha is expected to conform and the manner in which those tests should be carried out. The naphtha must contain not less than 72% by volume of methyl alcohol and not more than 12 grm. per 100 c.c. of aldehydes, acetone, and higher ketones estimated as acetone by Messinger's iodoform process, nor more than 3 grm. of esters estimated as methyl acetate by hydrolysis. Not more than 30 ml. of naphtha shall be required to decolourise an aqueous solution containing 0·5 grm. of bromine, and 5 ml. at least of deci-normal acid shall be required to neutralise 25 ml. of the spirit, when methyl orange is used as an indicator.

The proportion of methyl alcohol in wood-naphtha does not vary between very wide limits and it is by the recognition of this alcohol, therefore, that the presence of methylated spirits is usually indicated. For the detection of methyl alcohol in the presence of ethyl alcohol the differences in their physical properties may be utilised or recourse may be had to the differences in the chemical behaviour of derivatives or products of oxidation. One of the most important and reliable tests is that of Riche and Bardy, which depends on the ultimate formation of methylaniline violet and its deposition on wool (Compt. rend. 1875, **80**, 1076). As a preliminary test and one which may with advantage be incorporated in the Riche and Bardy process, the following will be found to be useful. About 10 ml. of the strong spirit freed, if necessary, from the essential oils, etc., by the salt-petroleum method and fractionated from potassium carbonate, is placed with 30 grm. of powdered iodine in a small round-bottomed flask which can readily be connected with a condenser. Two grm. of amorphous phosphorus are added and the resulting alkyl iodides distilled and collected under water in a small separator. When from 10 to 12 ml. have been collected, the iodides are washed with water, decolourised with dilute potash, and drawn off from the aqueous layer into a flask containing a little freshly heated potassium carbonate. After remaining an hour or so with occasional shaking, the potassium carbonate is removed by filtration and the boiling-point of the iodides carefully determined. Ordinary ethyl alcohol yields an iodide which has a constant boiling-point of 72°. The presence of methyl alcohol in the spirit depresses the boiling-point of the iodides, and reference to the following table will give a good approximation of the proportion of methyl alcohol present in the spirit.

Percentage of methyl alcohol by volume in the mixture of alcohols.	Temperature at which the first drop of iodides falls into the condenser.	Volume of distillate obtained below 72° from 10 ml. of the iodides. ml.
nil	70°	nil.
0·38	69°	0·2
0·94	65°	0·8
1·86	63°	2·2
2·77	62°	4·0
3·66	60°	5·0
4·55	58°	6·0
5·42	57°	6·2
6·26	56°	6·4
7·10	55°	6·5
10·00	52°	7·5

In doubtful cases, or when the initial boiling-point is below 70°, the first fraction of 3 ml. of distilled iodides is digested with an equal volume of aniline at a moderate temperature, and the Riche and Bardy method proceeded with After standing one hour, hot water is added to the crystalline mass and the mixture boiled for some minutes. Twenty-five ml. of strong potash solution are then added and the liberated oil washed with water. One ml. of this oil is intimately mixed with 10 grm. of a mixture consisting of 100 grm. dry quartz sand, 3 grm. of cupric nitrate, and 2 grm. of common salt, and the mixture introduced into a wide tube and heated for some hours at 90°–100°. The product is exhausted with warm alcohol and the extract filtered and made up to a volume of 100 ml.

If the original spirit contained ethyl alcohol only the colour of the liquid will be red but in the presence of 1% of methyl alcohol it has a distinct violet shade, whilst in the presence of 2% the violet is very decided and becomes more so as the proportion of methyl alcohol increases. Five ml. of the alcoholic extract are then mixed with water to a volume of 100 ml. and 2 ml. of this solution diluted with water to about 400 ml. The mixture is now heated to a temperature not exceeding 75°, and a length of Berlin wool, previously freed from grease by treatment with hot dilute potash, immersed in it for 30 minutes. If methyl alcohol was originally present, the fibre will become violet, the tint becoming more intense and increasing in depth with an increasing proportion of methyl alcohol. For purposes of comparison it is advisable to operate concurrently with a sample of rectified spirits known to be free from methyl alcohol.

Where a large number of samples has to be examined for the presence of methyl alcohol, the method of Denigès (Compt. rend. 1910, **150**, 832) is the most convenient. Positive results obtained thus are usually confirmed by the application of the more tedious Riche and Bardy process. Denigès' method is based upon the oxidation of methyl alcohol to formaldehyde and the detection of the latter by means of Schiff's reagent in the presence of sulphuric acid, which is introduced to prevent the development of colour with any acetaldehyde, formed from the ethyl alcohol during the oxidation.

A convenient quantitative method for the estimation of methyl alcohol or methylated spirits in a sample is that of Thorpe and Holmes (Chem. Soc. Trans. 1904, **85**, 1). This method depends upon the complete oxidation of methyl alcohol to carbon dioxide by means of chromic acid mixture, rectified spirits under the same conditions yielding only a small quantity of carbon dioxide equivalent to 0·01 grm. for each grm. of ethyl alcohol present.

Kollo and Crisan (Compt. rend. Soc. Biol. 1932, **109**, 795–6) suggest a microchemical method for the identification of methyl alcohol in the presence of ethyl alcohol, based upon the property of methone (5 : 5-dimethyldihydroresorcinol) to form, with aldehydes, methonic compounds which differ in their crystalline form and in their fusion and sublimation points. To 5 ml. of Beckmann's solution (5 grm. $K_2Cr_2O_7$ in 30 ml. of water and 2·8 ml. of concentrated sulphuric acid) 10 drops of the sample are added gradually and with constant shaking. After 5 minutes, 2 to 3 ml. are distilled off over a microburner. This distillate contains the aldehyde resulting from the oxidation of the alcohol. An excess of methone solution (0·5 part in 100 ml. of water) is added and the tube immersed in a boiling water bath for 5 to 10 minutes, at the end of which time a precipitate forms. The precipitate can then be separated and subjected to fractional microsublimation. F. G. H. T.

ALCOHOLOMETRY is the term applied to any process for determining the proportion of alcohol in a spirituous liquid. In simple mixtures of alcohol and water the specific gravity at a standard temperature affords an accurate index of alcoholic content and it is by this method that the determination of alcoholic strength for revenue and commercial purposes is usually carried out.

The specific gravity of a mixture of alcohol and water cannot be calculated from the respective gravities and comparative volumes of the two separate liquids, owing to the fact that on mixing the liquids contraction takes place, thus giving a volume of mixture smaller than the sum of the two separate volumes. In countries in which the revenue from spirit is of great importance it has been found necessary, therefore, to ascertain by experiment the specific gravities of mixtures of alcohol and water in all proportions and at various temperatures. These investigations have generally been carried out at the request of the governments interested and the tables thus prepared have been associated with the names of those entrusted with the investigations.

Thus in 1787 an act was passed by the British Parliament legalising the use of Clarke's hydrometer for the determination of alcoholic strengths but declared it expedient that investigations should be made in order that a better alcoholometric system might be introduced. In consequence of this declaration the Government invited the Royal Society to carry out the investigation. The invitation was accepted and the work placed in the hands of Sir Charles Blagden, Secretary of the Society, who was assisted first by Dr. Dollfuss for a short time and then by George Gilpin, clerk to the Society, who carried out most of the experimental work. The results were published in the Philosophical Transactions (1790–1794). They formed the basis of the tables used in this country in connection with Sikes' hydrometer for over a century and were later recognised by Mendeléeff, in the middle of the last century and by Thorpe, at the beginning of this, as so reliable that they were, in part, accepted as worthy of incorporation in their respective systems. At that time anhydrous alcohol had not been prepared and Blagden and Gilpin took as their strongest spirit one having a specific gravity of 0·825 at 15·6°/15·6° (60°/60°F.). This has an alcoholic strength of 92·55 by volume and 89·03 by weight. Similarly, the Prussian government ordered an investigation, which was carried out by Tralles (Gilb. Ann. 1811). He took the specific gravity of alcohol at 15·6°/15·6° to be 0·7946, equivalent, according to modern data, to 99·80% of alcohol by volume and 99·68% by weight. Incidentally he confirmed the accuracy of Blagden and Gilpin's data. He constructed tables which for upwards of sixty years formed the basis of the German alcoholometric system. Similar researches were carried out by Gay-Lussac (Paris, 1824), McCulloch (Washington, 1848), Baumhauer (Amsterdam, 1860), Mendeléeff (St. Petersburg, 1865), the Kaiserliche Normal-Eichungs-Kommission (Berlin, 1889), and the Bureau of Standards (Washington, 1913). In each case the results have been accepted by the respective government and incorporated in the official system of alcoholometry. Unofficial investigations were also carried out by Fownes (Phil. Trans. 1847), Drinkwater (Chem. Soc. Mem. 1848), and Squibb (Ephemeris, 1884), their results being entitled to consideration. Drinkwater prepared alcohol of a specific gravity 0·79381 at 15·6°/15·6° (in air). Squibb claimed to have prepared alcohol having a specific gravity as low as 0·7935, but this result has not been confirmed.

Of all these investigations probably one of the most comprehensive and exact was that of Mendeléeff. Although he obtained data for the whole range of alcoholic strengths, he was so well satisfied with the work of Blagden and Gilpin and Drinkwater that, for mixtures of low strengths, he adopted many of their values. The Kaiserliche Normal-Eichungs-Kommission, when carrying out their investigation for the German government, made a critical examination of Mendeléeff's final data and accepted them as the basis of the present German system of alcoholometry which replaced that of Tralles in 1887. Recently Koyalovich (Vsesoyuznuĭ Nauch Issledovatel Inst. Metrol. i Standartizatzin, 1933, No. 119) has given further confirmation to Mendeléeff's data.

In Great Britain the most complete investigation of modern times was that initiated by the Government early in the present century and carried out at the Government Laboratory by Sir Edward Thorpe, assisted by the writer and other members of his staff. After a close examination of all existing data, Thorpe decided to incorporate in his tables values from the tables of Blagden and Gilpin, Drinkwater, Mendeléeff and the German Commission. His tables were adopted by the Government and were legalised in 1916 under the Finance Act of 1907. The following summarised table is extracted from that published by Thorpe.

Specific gravity in air at $\frac{15\cdot6^\circ}{15\cdot6^\circ}$	Percentage of alcohol		Percentage of fiscal proof spirit	Specific gravity in air at $\frac{15\cdot6^\circ}{15\cdot6^\circ}$	Percentage of alcohol		Percentage of fiscal proof spirit
	by weight	by volume at 15·6°			by weight	by volume at 15·6°	
0·79359	100·00	100·00	175·35	0·898	58·93	66·67	116·81
0·794	99·87	99·92	175·21	0·900	58·06	65·83	115·33
0·796	99·22	99·52	174·52	0·902	57·18	64·98	113·84
0·798	98·57	99·12	173·80	0·904	56·31	64·13	112·35
0·800	97·91	98·70	173·07	0·906	55·42	63·26	110·82
0·802	97·25	98·28	172·33	0·908	54·54	62·39	109·29
0·804	96·57	97·84	171·56	0·910	53·65	61·51	107·74
0·806	95·89	97·39	170·77	0·912	52·77	60·63	106·20
0·808	95·20	96·93	169·96	0·914	51·88	59·74	104·63
0·810	94·50	96·45	169·13	0·916	50·98	58·83	103·05
0·812	93·80	95·97	168·28	0·918	50·08	57·92	101·43
0·814	93·08	95·47	167·41	0·91976	49·28	57·10	100·00
0·816	92·36	94·97	166·51	0·920	49·17	56·99	99·80
0·818	91·63	94·45	165·60	0·922	48·25	56·05	98·16
0·820	90·90	93·92	164·67	0·924	47·33	55·10	96·49
0·822	90·16	93·38	163·72	0·926	46·40	54·14	94·80
0·824	89·41	92·83	162·75	0·928	45·47	53·16	93·09
0·826	88·65	92·26	161·76	0·930	44·53	52·18	91·36
0·828	87·88	91·69	160·75	0·932	43·59	51·18	89·61
0·830	87·11	91·11	159·73	0·934	42·62	50·15	87·81
0·832	86·34	90·52	158·69	0·936	41·64	49·10	85·97
0·834	85·56	89·91	157·63	0·938	40·65	48·04	84·10
0·836	84·78	89·30	156·56	0·940	39·65	46·95	82·19
0·838	83·99	88·68	155·47	0·942	38·64	45·85	80·26
0·840	83·20	88·06	154·37	0·944	37·60	44·71	78·26
0·842	82·40	87·42	153·25	0·946	36·54	43·54	76·21
0·844	81·60	86·77	152·12	0·948	35·46	42·35	74·12
0·846	80·79	86·12	150·97	0·950	34·37	41·13	71·98
0·848	79·98	85·46	149·80	0·952	33·25	39·87	69·76
0·850	79·17	84·78	148·62	0·954	32·09	38·57	67·48
0·852	78·35	84·11	147·43	0·956	30·90	37·20	65·09
0·854	77·53	83·42	146·23	0·958	29·66	35·79	62·60
0·856	76·71	82·73	145·01	0·960	28·39	34·33	60·03
0·858	75·88	82·03	143·78	0·962	27·06	32·79	57·33
0·860	75·05	81·32	142·54	0·964	25·68	31·18	54·51
0·862	74·22	80·61	141·28	0·966	24·23	29·48	51·53
0·864	73·39	79·89	140·02	0·968	22·71	27·69	48·38
0·866	72·55	79·16	138·74	0·970	21·14	25·83	45·14
0·868	71·72	78·43	137·46	0·972	19·53	23·91	41·77
0·870	70·88	77·69	136·16	0·974	17·90	21·96	38·35
0·872	70·04	76·94	134·84	0·976	16·25	19·98	34·87
0·874	69·19	76·19	133·53	0·978	14·61	18·00	31·42
0·876	68·35	75·44	132·19	0·980	12·99	16·04	27·99
0·878	67·51	74·68	130·86	0·982	11·42	14·13	24·66
0·880	66·66	73·91	129·50	0·984	9·91	12·29	21·44
0·882	65·81	73·13	128·14	0·986	8·46	10·51	18·34
0·884	64·96	72·34	126·77	0·988	7·08	8·80	15·38
0·886	64·10	71·55	125·37	0·990	5·76	7·18	12·53
0·888	63·24	70·75	123·97	0·992	4·51	5·63	9·82
0·890	62·38	69·95	122·56	0·994	3·31	4·14	7·24
0·892	61·52	69·14	121·14	0·996	2·17	2·71	4·73
0·894	60·66	68·33	119·70	0·998	1·07	1·34	2·33
0·896	59·80	67·50	118·26	1·00000	0·00	0·00	0·00

It will be observed that a column is devoted to percentages of "proof spirit." This term has subsisted since the earliest attempts to set up a system of spirit assessment in this country.

Although reference had been made to proof strengths in earlier enactments it was in the Spirits Act of 1816 that the first attempt was made to give a clear legal definition of "proof spirit." There it was defined as "that which, at the Temperature of Fifty-one Degrees by Fahrenheit's Thermometer, weighs exactly twelve-thirteenths of an equal measure of distilled water." Although the temperature of water is not defined there is conclusive documentary evidence that it was intended to be at the same temperature. According to Thorpe's tables this mixture of alcohol and water has a specific gravity of 0·91976 at 15·6°/15·6° and contains 49·28% of anhydrous alcohol by weight and 57·10% by volume at 15·6°C. Spirits which contain a greater proportion of alcohol than is contained in proof spirit are said to be overproof (o.p.), whilst those which contain a smaller proportion are said to be underproof. Proof strengths can also be expressed as a percentage as in the above table. In this form the overproof strengths are an expression of the volume which would be obtained by diluting 100 volumes of the spirit with water down to proof strength. Similarly, the percentages below proof strength give the volume of proof spirit which would be obtained if the alcohol contained in 100 volumes of the spirit were diluted with water to proof strength. Thus, by reference to the above table, it will be seen that absolute alcohol, having a specific gravity of 0·79359 at 15·6°/15·6°, has a proof strength of 175·35 or 75·35 o.p., which means that 100 volumes of absolute alcohol diluted with water to 175·35 volumes gives proof spirit. Proof strengths are based upon volume percentages of alcohol at 50°F. (10°C.). Owing to the difference in the coefficients of expansion of the two ingredient liquids, the volume percentage of a spirituous mixture varies with thermal changes. For fiscal purposes, however, proof strengths are not considered to vary and a spirit will have the same strength whatever the temperature. Although this feature of the British system has been severely criticised on scientific grounds, it has the undoubted merit of easy adaptability to commercial and revenue requirements.

In the above table specific gravities are correlated with percentages of proof spirit and of alcohol by weight and by volume at 15·6°. The specific gravities represent the ratio of the weight of a given volume of spirit to the weight of the same volume of water at 15·6°, both determined in air under the same atmospheric conditions. They may be converted to specific gravities in vacuum by means of the expression :

$$\frac{\delta+0\cdot0012}{1\cdot0012}$$

As a supplement to the above tables, and for use when the prevailing temperature is so high as to render difficult the determination of specific gravity at 60°F., the writer has compiled tables correlating specific gravities at 80°F. with percentages of proof spirit and of alcohol by weight. These tables were legalised by regulations published by the Commissioners of Customs and Excise in 1933 under the Finance Act of 1907. The following is a brief summary of these tables :

Specific gravity in air at 80°/80° Fahr.	Percentage of proof spirit.	Percentage of alcohol by weight.
0·786	175·34	99·99
0·790	173·94	98·69
0·800	170·10	95·32
0·810	165·74	91·75
0·820	160·92	88·01
0·830	155·67	84·13
0·840	150·05	80·15
0·850	144·08	76·08
0·860	137·83	71·96
0·870	131·32	67·80
0·880	124·55	63·59
0·890	117·52	59·35
0·900	110·17	55·05
0·910	102·51	50·68
0·913162	100·00	49·28
0·920	94·44	46·21
0·930	85·88	41·60
0·940	76·60	36·74
0·950	66·41	31·56
0·960	54·75	25·80
0·970	41·15	19·23
0·980	26·31	12·20
0·990	12·28	5·64
1·000	0·00	0·00

It may be observed that the specific gravity of absolute alcohol at 80°/80° is 0·78598.

Although it is probable that the density of a spirituous liquid can be determined more accurately by a pycnometer than by other means, in practical operations where regard must be had to convenience it is often preferable to employ one of the many hydrometers or alcoholometers, the stems of which are variously graduated to show densities, percentages of alcohol by weight or by volume, or again arbitrary indications which can be interpreted by suitable tables.

Since the year 1816 Sikes' hydrometer has been the legal instrument for ascertaining the strength of spirits for revenue purposes in Great Britain and Ireland and throughout the Empire. It is made of brass, usually gilded, and consists of a hollow sphere, provided at one pole with a graduated rectangular stem uniform in section, and at the other with a conical spindle terminating in an oval counterpoise to give stability to the instrument when floating in a liquid, and also to serve as an attachment for various poises. The graduated portion of the stem contains ten principal divisions, which are equal in length and marked "0" at the upper and "10" at the lower end, and between these points the stem is subdivided to two-tenths of a division. When the instrument is floating at the "0" mark in spirit at a temperature of 15·6° it indicates a strength of 66·7 overproof, or 92·50% of alcohol by weight, whilst the "10" mark corresponds to a strength of 58 overproof, or 86·11% of alcohol (by weight). For strengths weaker than these a series of nine poises or weights are used numbered consecutively from 10 to 90. The poises are made of hammered brass, usually gilded, and can be attached, by means of a slot in the poise, to the spindle of the hydrometer. The series of principal divisions can thus be repeated ten times, reading from "0" to "100," which latter indication represents distilled water. The readings are interpreted into proof strengths by means of tables which are arranged so as to identify a sample of spirit at any temperature between −1·1° (30°F.) and +37·8° (100°F.). These tables replaced those originally compiled by Sikes. They were prepared by Thorpe during his investigation to which reference has already been made and were legalised in 1915.

As stated above, the highest strength indicated by Sikes' hydrometer is 92·50% of alcohol by weight. Although this strength was sufficiently high for practical purposes when Sikes' hydrometer was introduced, the commercial production of spirits of higher strengths rendered necessary an additional instrument extending the range towards absolute alcohol. Thorpe, therefore, included in his system the "A" hydrometer, similar in design and marking to the Sikes' hydrometer but without weights. The "10" mark at the bottom of the graduated stem indicated at 15·6° a strength of 66·7 overproof or 92·50% of alcohol, the strength proper to the "0" mark on Sikes' hydrometer. The "0" mark corresponded, at 15·6°, to a strength of 73·5 overproof or 98·24% of alcohol. At 26·7°C. (80°F.) the strength at "0" indication was 70·0 overproof or 95·2% of alcohol by weight, and at 37·8°C. (100°F.) it was 65·9 overproof or 91·9% of alcohol by weight. In course of time this instrument also became inadequate owing to the manufacture of absolute alcohol on a commercial scale. This was particularly the case during the summer months in Great Britain and throughout the year in tropical countries. The writer, therefore, devised a further instrument—Sikes' "B" hydrometer. This is similar in design to the "A" hydrometer, but so calibrated that with a poise attached it corresponds to that instrument, whilst without the poise it covers a range of densities in continuation of the "A" and including absolute alcohol up to 84°F. Tables for use with this hydrometer were legalised by the Strength and Weight of Spirits Ascertainment Regulations, 1930, made by the Commissioners of Customs and Excise under the Finance Act of 1907.

Other Countries.—In France Gay-Lussac's original alcoholometer and tables, which had been in use for sixty years, were corrected in 1884 by data based upon densities of aqueous alcoholic mixtures determined by the "Bureau national des poids et mésures." The density of anhydrous alcohol at 15°/15° is given as 0·79433 in vacuum, as against 0·7947 assumed by Gay-Lussac, and the difference between the old and the new official instruments reaches a maximum of 0·4% for spirits containing from 20 to 21% by volume. Thus 20°, at a temperature of 15° on the new legal centesimal alcoholometer, indicates spirit containing 20% by volume of alcohol, and corresponds to 20·4° on Gay-Lussac's original instrument. The French spirit tables indicate, at temperatures extending from 0° to 30°, the percentage by volume of alcohol which a liquid contains at 15°.

In Spain and South America Cartier's areometer and tables, which were previously used in France, are officially recognised. Its stem is graduated from 10 to 45 in divisions of equal length, and indicates the concentration of a spirituous liquid by arbitrary degrees, which serve as spirit strengths for charging duty. In Switzerland, Beck's hydrometer, a modification of Cartier's, is used. It floats at the lowest indication in distilled water at 12·5° (10°R.).

In Italy Tralles' alcoholometer is the official instrument for alcoholic assessment. It is made of glass and at the standard temperature of 15·6° indicates directly the number of volumes of alcohol contained in 100 volumes of the spirit when measured at the same temperature. Indications at other temperatures are corrected by means of tables to true percentages by volume at 15·6°.

Tralles' alcoholometer and tables are also used in Russia for commercial purposes, but for revenue assessment a metal hydrometer with nine poises, similar in character to Sikes' hydrometer, is used. The indications, although extending from 0 to 100, are in reverse order to those of Sikes, however, the "100" representing strong spirit and the "0" corresponding with water. The intermediate indications have no true significance as alcoholic strengths, which are ascertained by reference to appropriate tables referred to Tralles' values at 15·6°.

Previous to the year 1887 Tralles' instrument was also used in Germany. It has been replaced by a system of alcoholometry based by the Kaiserliche Normal-Eichungs-Kommission on the data obtained by Mendeléeff in his investigation of 1865. The instruments are made of glass and indicate, at 15°, percentages of alcohol by weight, conversions from other temperatures being made by reference to tables. Duty is, however, charged on the volume of anhydrous alcohol present in a spirit when measured at 15·6°. This system is therefore analogous to the British, with the exception that the dominant temperature at which British proof strengths are based upon percentages of alcohol by volume is 10°.

In Austria an alcoholometer closely resembling that of Tralles and indicating percentages of alcohol by volume at 15° is used. Its indications are uniformly higher than those of Tralles to the extent of from $\frac{1}{10}$ to $\frac{2}{10}$%. Readings on this instrument are taken at the highest point of the capillary meniscus, which extends 1–2 mm. on the stem above the normal surface of the liquid.

An indispensable step to a correct assay of spirit is the removal of any foreign matter which may be in solution in the alcoholic mixture. In the case of potable spirits, wines, liqueurs and similar preparations the spirit is freed from saccharine and other dissolved matter by distillation. The amount by which the true alcoholic strength of brandy or rum differs from the apparent strength, as indicated

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·6°	Alcohol by weight (Germany)	Alcohol by volume		Russia	Holland	Spain (Cartier)	Switzerland (Beck)
				at 15° (France)	at 15·6° (Tralles)				
	Overproof								
B.7	75·2	200·0	99·8	99·9	99·9	—	—	—	—
B.8	74·6	199·5	99·3	99·6	99·7	—	—	—	—
B.9	74·1	198·9	98·8	99·3	99·4	—	—	—	—
A.0 = B.10	73·5	198·2	98·2	98·9	99·1	—	25·3	43·5	42·6
A.1	72·9	197·5	97·7	98·6	98·8	—	25·0	43·2	—
A.2	72·2	196·8	97·2	98·2	98·4	—	—	—	41·8
A.3	71·6	196·1	96·6	97·8	98·0	—	24·5	—	—
A.4	71·0	195·3	96·1	97·5	97·7	—	—	42·2	40·9
A.5	70·3	194·6	95·5	97·1	97·3	—	24·0	—	—
A.6	69·6	193·8	94·9	96·7	96·9	—	—	—	—
A.7	68·9	193·0	94·3	96·3	96·5	—	23·5	41·2	39·6
A.8	68·2	192·2	93·7	95·9	96·1	—	—	—	—
A.9	67·5	191·3	93·1	95·4	95·6	99·2	23·0	—	—
A.10=0	66·7	190·4	92·5	95·0	95·2	98·3	—	40·1	38·3
1	66·0	189·6	91·9	94·7	94·8	—	22·5	—	—
2	65·2	188·7	91·3	94·2	94·3	96·3	—	—	—
3	64·4	187·7	90·7	93·8	93·9	—	22·0	39·1	37·1
4	63·6	186·8	90·0	93·3	93·4	94·4	—	—	—
5	62·8	185·8	89·4	92·8	92·9	—	21·5	—	—
6	61·9	184·9	88·8	92·3	92·4	92·4	—	38·1	35·8
7	61·1	183·9	88·1	91·8	91·9	—	21·0	—	—
8	60·2	182·9	87·5	91·3	91·4	90·5	—	—	34·9
9	59·3	181·8	86·8	90·8	90·9	—	20·5	37·2	—
10	58·4	180·8	86·1	90·3	90·4	88·5	—	—	34·1
11	57·6	179·9	85·6	89·9	90·0	—	20·0	—	—
12	56·7	178·9	84·9	89·4	89·5	86·6	—	36·2	—
13	55·7	177·9	84·2	88·8	88·9	—	19·5	—	32·9
14	54·8	176·8	83·5	88·3	88·4	84·6	—	—	—
15	53·8	175·7	82·8	87·7	87·8	—	19·0	35·2	32·0
16	52·9	174·6	82·1	87·2	87·3	82·6	—	—	—
17	51·9	173·4	81·4	86·6	86·7	—	18·5	—	—
18	50·9	172·3	80·7	80·6	86·1	80·6	—	34·2	30·8
19	49·9	171·1	80·0	85·5	85·6	—	18·0	—	—
20	48·9	170·0	79·3	84·9	85·0	78·7	—	—	30·0
21	47·9	168·8	78·6	84·3	84·4	—	17·5	—	—
22	46·8	167·7	77·9	83·8	83·9	76·7	—	33·0	—
23	45·8	166·5	77·2	83·1	83·2	—	17·0	—	28·8
24	44·7	165·3	76·5	82·5	82·6	74·8	—	—	—
25	43·6	164·0	75·8	81·9	82·0	—	—	32·0	28·0
26	42·5	162·7	75·0	81·3	81·4	72·8	16·3	—	—
27	41·4	161·5	74·3	80·6	80·7	—	—	—	—
28	40·3	160·2	73·6	80·0	80·1	70·9	15·9	31·1	26·8
29	39·1	158·9	72·8	79·4	79·5	—	—	—	—
30	38·0	157·6	72·1	78·7	78·8	68·9	15·4	—	26·0
31	36·9	156·3	71·3	78·1	78·2	—	—	30·1	—
32	35·7	155·0	70·6	77·4	77·5	67·0	14·9	—	—
33	34·6	153·7	69·9	76·8	76·9	—	—	—	24·8
34	33·4	152·4	69·1	76·1	76·2	65·0	14·5	29·2	—
35	32·2	151·0	68·4	75·4	75·5	—	—	—	24·0
36	31·0	149·6	67·6	74·7	74·8	63·1	14·0	—	—
37	29·8	148·2	66·8	74·0	74·1	—	—	28·2	23·2
38	28·5	146·8	66·1	73·3	73·4	61·1	13·5	—	—
39	27·3	145·4	65·3	72·6	72·7	—	—	—	—
40	26·0	144·0	64·5	71·9	72·0	59·2	13·1	—	22·0
41	24·8	142·6	63·8	71·2	71·3	—	—	27·0	—
42	23·6	141·1	63·0	70·5	70·6	57·2	—	—	—
43	22·3	139·7	62·2	69·7	69·8	—	12·4	—	20·9
44	21·0	138·2	61·4	69·0	69·1	55·3	—	26·1	—
45	19·7	136·7	60·6	68·3	68·4	—	11·9	—	20·1
46	18·3	135·2	59·8	67·5	67·6	53·3	—	—	—
47	17·0	133·7	59·0	66·7	66·8	—	11·5	25·2	—

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·6°	Alcohol by weight (Germany)	Alcohol by volume		Russia	Holland	Spain (Cartier)	Switzerland (Beck)
				at 15° (France)	at 15·6° (Tralles)				
	Overproof								
48	15·6	132·1	58·2	65·9	66·0	51·3	—	—	18·9
49	14·3	130·6	57·4	65·1	65·3	—	11·0	—	—
50	12·9	129·0	56·6	64·3	64·5	49·4	—	—	—
51	11·5	127·4	55·8	63·5	63·7	—	10·5	24·0	17·8
52	10·1	125·8	55·0	62·7	62·9	47·4	—	—	—
53	8·7	124·2	54·2	61·9	62·1	—	10·1	—	17·0
54	7·3	122·6	53·4	61·1	61·3	45·5	—	23·1	—
55	5·8	120·9	52·5	60·2	60·4	—	—	—	—
56	4·4	119·2	51·7	59·4	59·6	43·5	9·4	—	15·9
57	2·9	117·5	50·9	58·5	58·7	—	—	22·2	—
58	1·4	115·7	50·0	57·7	57·9	41·5	9·0	—	15·1
	Underproof								
59	0·2	114·0	49·2	56·8	57·0	—	—	—	—
60	1·7	112·2	48·3	55·9	56·1	39·5	—	21·3	—
61	3·3	110·5	47·5	55·0	55·2	—	8·3	—	14·0
62	4·8	108·7	46·6	54·1	54·3	37·6	—	—	—
63	6·4	106·9	45·8	53·2	53·4	—	7·9	—	13·3
64	8·1	105·0	44·9	52·3	52·5	35·6	—	20·1	—
65	9·7	103·1	44·0	51·3	51·5	—	—	—	—
66	11·4	101·2	43·1	50·4	50·6	33·6	7·2	—	12·2
67	13·1	99·3	42·1	49·4	49·6	—	—	—	—
68	14·9	97·2	41·1	48·4	48·6	31·6	6·8	19·0	—
69	16·7	95·1	40·2	47·3	47·5	—	—	—	11·0
70	18·6	93·0	39·2	46·3	46·5	29·7	—	—	—
71	20·5	90·8	38·2	45·2	45·4	—	6·1	18·1	—
72	22·4	88·6	37·2	44·1	44·3	27·7	—	—	9·9
73	24·4	86·4	36·2	43·0	43·2	—	5·7	—	—
74	26·4	84·2	35·2	41·9	42·1	25·7	—	—	—
75	28·5	81·8	34·1	40·7	40·9	—	—	16·9	8·8
76	30·7	79·4	33·0	39·5	39·7	23·7	5·1	—	—
77	32·9	76·9	31·9	38·3	38·5	—	—	—	8·1
78	35·3	74·3	30·7	36·9	37·1	21·8	—	16·1	—
79	37·7	71·4	29·5	35·5	35·7	—	4·4	—	—
80	40·3	68·5	28·2	34·0	34·2	19·8	—	—	7·0
81	42·9	65·4	26·9	32·5	32·7	—	4·0	—	—
82	45·7	62·3	25·6	31·0	31·2	17·9	—	15·0	—
83	48·6	58·9	24·2	29·3	29·5	—	3·6	—	6·0
84	51·7	55·4	22·7	27·5	27·7	15·9	—	—	—
85	54·8	51·7	21·1	25·6	25·8	—	—	14·1	—
86	58·2	47·9	19·5	23·7	23·9	13·9	3·0	—	4·9
87	61·5	44·1	18·0	21·8	22·0	—	—	—	—
88	65·0	40·2	16·4	19·9	20·1	11·9	—	13·3	—
89	68·4	36·2	14·7	18·0	18·1	—	2·3	—	3·8
90	71·9	32·2	13·1	16·0	16·1	9·9	—	—	—
91	75·2	28·4	11·5	14·1	14·2	—	1·9	12·4	3·1
92	78·4	24·7	10·0	12·3	12·4	7·9	—	—	—
93	81·4	21·3	8·6	10·6	10·7	—	1·5	—	—
94	84·4	17·9	7·2	8·9	9·0	6·0	—	11·6	2·1
95	87·3	14·6	5·8	7·2	7·3	—	—	—	—
96	90·0	11·4	4·6	5·6	5·7	4·0	0·9	—	—
97	92·6	8·4	3·4	4·1	4·2	—	—	10·8	1·0
98	95·1	5·6	2·2	2·7	2·8	2·0	—	—	—
99	97·6	2·8	1·1	1·4	1·4	—	—	—	—
100	100·0	0·0	0·0	0·0	0·0	0	0	10·1	0·1

by the hydrometer or density determination, is termed the "obscuration." The distillation of a strong spirituous liquid into its own volume, so as to obtain an accurate determination of the amount of alcohol present, is impracticable with the apparatus and the methods of distillation commonly used, so that, although it is possible to distil without loss spirits of underproof strength into the same volume, it is necessary to dilute overproof spirits and distil into two, three, or four times the original volume. In the British system, whilst the measurement of volume takes place at 60°F., proof spirit is based upon percentage of alcohol by volume at 50°F. Arithmetical multiplication of the proof strength of the diluted solution by a factor representing the dilution does not therefore give the correct proof strength of the original spirit. In order to eliminate the error which would be introduced Thorpe incorporated in the British system tables for double, treble and quadruple dilutions, correlating the specific gravity of the dilute solution with the proof strength of the original spirit.

While the strength of spirituous preparations can often be ascertained by the determination of the specific gravity or the refraction of the distillate obtained by simple distillation, many preparations contain volatile ingredients other than ethyl alcohol, which render necessary some more complicated method. In the case of medicinal preparations, flavouring essences and other preparations, which yield distillates containing essential oils and volatile substances, the sample or distillate is mixed with water in a separator, so that the mixture shall contain not more than 20–25% by volume of alcohol, and common salt is added in quantity sufficient to saturate the liquid. The mixture is then shaken vigorously with 50–100 c.c. of light petroleum and, after remaining a short time, the aqueous layer is extracted, if necessary, a second time with petroleum (for instance, when chloroform or ether is present), and finally drawn off into a flask and distilled. In the case of soap liniments and similar preparations, dilute sulphuric acid is used instead of salt and the aliphatic acids and volatile matters removed by petroleum before distilling (Thorpe and Holmes, Chem. Soc. Trans. 1903, **83**, 314). Preparations containing iodine are decolourised with sodium thiosulphate and excess of caustic soda added to prevent decomposition of the tetrathionate during distillation. Similarly, volatile acids must be neutralised, and ammoniacal liquids distilled from dilute sulphuric acid solution. A micro-determination of ethyl alcohol is based upon the colorimetric measurement of the excess of potassium bichromate used in oxidation of the alcohol, a sensitive photoelectric colorimeter being used with monochromatic light (Fonteyne and de Smet, Mikrochem. 1933, **13**, 289).

For the estimation of ethyl alcohol in fusel oil or liquids containing fusel oil, the salt-petroleum process may be employed but as the higher alcohols cannot be wholly eliminated by this method the specific refraction of the distillate is determined by the Zeiss immersion refractometer. The refractions of mixtures of ethyl alcohol and water have been determined at various temperatures by Wagner and Schultze (Z. anal. Chem. 1907, **46**, 508) and others, and a close approximation to the true alcoholic content of a fusel oil mixture, treated as above described, can be obtained by applying to the apparent percentage by volume of alcohol, as indicated by the specific gravity of the distillate, a subtractive correction of 0·5% for each degree of difference between the refractometer reading as found at 15·6° and that required for a mixture of ethyl alcohol and water corresponding to the ascertained density. This method of eliminating foreign matters in spirit assaying, from a knowledge of their influence on the specific refractions of aqueous alcoholic mixtures, is capable of wide application, and has been utilised, for instance, by Leach and Lythgoe (J. Amer. Chem. Soc. 1905, **27**, 964) for determining the proportion of methylated spirit in a spirituous liquid (*v.* REFRACTOMETER). Newton and Munro suggest a formula in which they use the refractometer reading and thus can, within reasonable limits, ascertain the alcoholic strength and extract content of wine. In the presence of methyl alcohol the ethyl alcohol can be oxidised with potassium dichromate and sulphuric acid, refluxed and then steam-distilled. The resultant acetic acid is titrated against $N/1$ soda solution. This method has been developed and improved by Maricq (Bull. Soc. chim. Belg. 1931, **40**, 333). A colorimetric method depends upon the determination of the total apparent alcoholic strength due to the two alcohols and the separate estimation of the methyl alcohol. A small portion of the distillate is treated with $KMnO_4$ and H_3PO_4, excess of the former being afterwards eliminated by the addition of a solution containing oxalic acid in dilute sulphuric acid. A modified Schiff's reagent is then added and the blue colour which develops matched against standard solutions of methyl alcohol similarly treated (Denigès, Compt. rend. 1910, **150**, 832; Simmonds, Analyst, 1912, **37**, 16; Georgia and Morales, Ind. Eng. Chem. 1926, **18**, 304). From known mixtures of ethyl alcohol and water and methyl alcohol Mortimer (Trans. Illinois State Acad. Sci. 1931, **24**, 279) has prepared a table showing variation in refractometer reading with composition for the two alcohols. From this table he obtained a set of factors by means of which percentages of the alcohols in a mixture can be calculated.

In the presence of *iso*propyl alcohol the method of Adams and Nicholls (Analyst, 1929, **54**, 2) depends upon oxidation with potassium bichromate. The resultant mixture of acetic acid and acetone is distilled, the distillate being neutralised quantitatively, giving the acetic acid and thence the ethyl alcohol. The neutralised liquid is redistilled, giving the acetone, which is estimated by gravity or colorimetrically. Macoun (J.S.C.I. 1928, **49**, 43) suggests the estimation of ethyl alcohol in the presence of acetone by the condensation of the acetone in alkaline solution with benzaldehyde to form dibenzylideneacetone. The excess of benzaldehyde and the alcohol are removed by distillation and the distillate is treated with aniline phosphate and subjected to a benzene-petroleum-salt separation, and finally with ammoniacal silver nitrate. By a slight modification this method can be used in the presence of methyl ethyl ketone.

The estimation of ethyl alcohol in preparations such as cellulose paints and nail polishes containing toluene, butyl alcohol, cellulose and plasticisers presents considerable difficulty. A convenient method is based upon the formation of azeotropes, as suggested by Lecat ("L'Azéotropisme," Bruxelles, 1918). The mixture may be diluted with benzene or toluene and distilled and the distillate similarly diluted. The solution is then slowly fractionated up to 90°C. and the distillate subjected to a brine separation with petroleum ether. If acetic ester is present the distillate, after the alcohol has been washed out, is treated with toluene and sodium hydroxide to saponify the ester and then redistilled. After further treatment with brine and redistillation, the alcohol is calculated to acetic ester. A resin test (*v.* Alcohol) should always be carried out on the final distillate to prove the presence of ethyl alcohol.

The probably increasing use of ethyl alcohol mixed with petrol or benzol or both as a motor spirit renders of importance the method proposed by J. Zdárský (Chem. Obzor, 1931, **6**, 297, 326) for the determination of ethyl alcohol and water in such mixtures. A known quantity of the mixture is shaken with calcium chloride solution in a graduated separating funnel. The calcium chloride solution is transferred to a distilling flask and the operation repeated with further portions of the calcium chloride solution. The residue of oil is a function of the amount of petrol or benzol present in the original mixture. The solution in the flask is distilled and the quantity of ethyl alcohol determined by specific gravity of the distillate in the usual manner.
F. G. H. T.

ALCOHOLS FOR MOTOR FUELS. It is due to insistent nationalistic efforts that alcohol is playing its part as motor fuel. Owing to the incidence of taxation a home-produced fuel obtains a definite preference, and it is practically certain that without this preference such a substitute fuel with its lower calorific value would only be employed in special cases where high anti-knock properties are essential. The only alcohols actually concerned in practice as fuels are methanol (methyl alcohol) and ethanol (ethyl alcohol).

The production of methanol from water gas is practised extensively and a variety of catalysts are employed, such as zinc oxide, zinc chromate, zinc and copper oxides, and basic zinc chromates.

The production of methyl alcohol averages about 15 million gallons per annum. This should be compared with the production of petroleum spirit, which amounts to 160,000 million gallons a year. For racing purposes methanol has been used as a blend with benzol and petrol, but it suffers from lack of solubility and some such solvent as aromatic hydrocarbons or higher alcohols is necessary to achieve a permanent blend. On the other hand, the anti-knock value is high.

For production of ethanol in Europe, the sole method is fermentation ; sugars and starches and celluloses have been made use of in this direction.

From the point of view of cost, it is fair to say that no country has yet produced alcohol on a commercial scale that will effectively compete with petroleum, and its use is only justified when a special degree of anti-knock value is required. Many of the European countries, notably France and Germany, as a means of assisting agriculture and from the wish to be as far as possible independent of foreign supplies, have made it compulsory to add alcohol to petroleum spirit. Corresponding attempts have failed in America because of the obviously greater difference between the price of the two commodities. Whilst the anti-knock value of alcohol is a definite asset, its lower calorific value and its hygroscopic nature are serious drawbacks. In the earlier days of alcohol blends when 95% ethanol was employed, there was considerable trouble with the separation of an aqueous layer. This is largely avoided to-day by the utilisation of very much stronger alcohol closely approximating 100%. Where there is a copious supply of ethylene as, for example, from the cracking process, the method of hydration of this hydrocarbon is practised, and it appears that in the United States the alcohol from ethylene is cheaper to produce than the corresponding fermentation product. The hydration process may be carried out by direct addition of water, for example at 450°C., or in the presence of high-pressure steam over catalysts, *see* Alcohols produced by synthesis from petroleum.

The anti-knock effectiveness of both ethanol and methanol can be taken as approximately twice that of benzol.
A. E. D.

ALCOHOLS PRODUCED BY SYNTHESIS FROM PETROLEUM. Reference should be made to the very comprehensive treatment of this subject in "The Chemistry of Petroleum Derivatives," by Carleton Ellis (Chemical Catalog Co., New York, 1934), and in a series of articles in "The Science of Petroleum" (Oxford University Press, 1936).

The synthesis of alcohols technically is achieved by the hydration of olefines or by the hydrolysis of chloro-derivatives.

Alcohols derived from Olefines.—Usually the hydration process is effected by means of relatively concentrated sulphuric acid and the subsequent hydrolysis of the alkyl sulphuric acid thus produced. On the other hand, direct hydration may be carried out in the presence of a catalyst which may be composed of non-volatile acids or anhydrides, *e.g.* phosphoric acid carried on an inert material. Some of the very early work is due to Brooks and Humphrey (J. Amer. Chem. Soc. 1918, **40**, 822).

Considering some practical examples, ethylene may be converted into ethyl alcohol by direct contact of a mixture of ethylene and steam counter-current to a hot stream of dilute sulphuric acid in a column. The hot acid is withdrawn from the base, while alcohol, water and unchanged ethylene are removed from the top of the column.

In connection with contact processes over catalysts reference should be made to the work of Horsley (B. 1932, 670), in which a mixture of ethylene and steam under pressure is heated in contact with phosphate catalysts, notably cadmium acid phosphate. Presumably in this case an intermediate ethyl phosphate is produced. It is interesting to note that the same author purified ethylene derived from cracking operations from the accompanying higher homologues by polymerising the latter over the same catalyst, but under conditions which left the ethylene unchanged.

In the case of propylene again, phosphate catalysts have been found sufficiently reactive, and Horsley (B. 1932, 1071) describes the reaction of equal volumes of steam and propylene over boron phosphate with the formation of *iso*propyl alcohol, and a similar degree of conversion in the case of acid cadmium phosphate.

*iso*Propyl alcohol is produced industrially and on a considerable scale by bringing propylene into contact with concentrated sulphuric acid at low temperatures in the presence of a non-reactive liquid absorbent. The resulting acid liquid is hydrolysed and may be used directly to make acetates or other esters by reaction with the sodium salt of the corresponding acid (*see* Ellis, Amer. Chem. Abstr. 1923, **17**, 3248). *iso*Butylene very readily polymerises to the dimeride under these conditions. In general the hydration reaction is reversible, but the higher olefines, *e.g.* amylene, are hydrated fairly readily in the presence of dilute mineral acids, whereas ethylene and propylene are more resistent. Generally, hydration is favoured by low temperatures, high pressures and effective catalysts. To increase the effectiveness of sulphuric acid as a catalyst it has been shown that small concentrations of silver sulphate are of value. Furthermore, direct hydration is favoured by the use of acids sufficiently concentrated to yield alkyl esters, but not strong enough to bring about polymerisation. As an example, *iso*butene cooled and dissolved in kerosene is treated with 50% sulphuric acid, further cooled to 0°C., and agitated for several hours. At the end of this period the reaction mixture is separated into a top kerosene layer and a bottom acid layer, which is hydrolysed by cooled alkali, and yields tertiary butyl alcohol on distillation.

By this procedure butene-1 and butene-2 are unaffected. Butene-2 yields secondary butyl alcohol with moderately concentrated acid. As before, the strong acid brings about polymerisation.

In the case of the pentenes polymerisation is liable to be brought about by acid over 50% strength.

Catalysts that have been suggested other than sulphuric acid and phosphoric acid are borax, molybdates, tungstates, vanadates and arsenates.

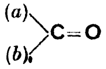
Alcohols derived from Chloro-Derivatives.—Most of this side of alcohol production is due to the work of the Sharples Corporation in Philadelphia, and to a large extent pentane has been used as the raw material.

For general methods of chlorination, reference should be made to "The Chemistry of Petroleum Derivatives," by Carleton Ellis, but an example may be given. In the Sharples plant a mixture of *n*- and *iso*-pentane is chlorinated in the vapour phase and in the dark. The product is continuously fractionated and a mixture of amyl chlorides eventually obtained. For the preparation of the most important products, amyl alcohol and amyl acetate, the mixed chlorides are hydrolysed with caustic soda, yielding the following mixture of alcohols: methyl propyl carbinol, diethyl carbinol, *iso*-butyl carbinol, secondary butyl carbinol, methyl *iso*propyl carbinol, dimethyl ethyl carbinol, amylene being a by-product of the hydrolysis. The acetate and a wide variety of esters made from these mixed alcohols are important as solvents and plasticisers. A. E. D.

ALCORNIN or **ALCORNOL.** An alcohol, $C_{22}H_{34}O$, m.p. 205°, and $[\alpha]_D+33{\cdot}83°$, of the nature of phytosterol, found in Alcornoco bark (Hartwich and Dünnenberger, Arch. Pharm. 1900, **238**, 341).

ALDEHYDE GREEN. The formation of this member of the triphenylmethane series, of doubtful constitution, was due to the action of a photographer who sought to fix the rather fugitive violet known as Hofmann's Violet (*q.v.*) by means of sodium thiosulphate, in the same manner as the image is fixed on the photographic plate. The outcome was to change the violet to a green. The colour had some vogue at the time, but is chiefly of interest as being the first green synthetic colouring matter to be produced.

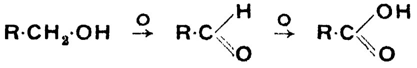
ALDEHYDES. Aldehydes (in common with ketones) are characterised by the presence of the carbonyl group:



$$\begin{matrix}(a)\diagdown \\ \quad\;\; C{=}O \\ (b)\diagup\end{matrix}$$

In the case of aldehydes, one valency (*a*) is linked to hydrogen; the second valency (*b*) to a hydrocarbon radical or a simple derivative thereof, with the exception of the first member of the series, formaldehyde, which is abnormal. as both the valencies (*a*) and (*b*) are attached to hydrogen.

Aldehydes form a class of compounds intermediate between the primary alcohols and the carboxylic acids:



$$R{\cdot}CH_2{\cdot}OH \overset{O}{\rightarrow} R{\cdot}C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix} \overset{O}{\rightarrow} R{\cdot}C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix}$$

They may be formed by the regulated oxidation of the primary alcohol; on further oxidation they pass to the acid.

Aldehydes are usually named from the acid into which they may be converted on oxidation, or by the addition of the suffix "al" to the hydrocarbon. The name aldehyde is an abbreviation of *alcohol dehydrogenatum.*

While many of the reactions of the aliphatic and aromatic aldehydes are similar, with certain reagents this is not the case, and different products are obtained.

Preparation.—(1) By the oxidation of the primary alcohols. This may be carried out by passing the vapour of the alcohol mixed with air over a suitable catalyst; formaldehyde may be prepared in this way by passing air and methyl alcohol over heated copper:

$$CH_3{\cdot}OH \overset{O}{\rightarrow} H{\cdot}CHO$$

The oxidation may also be carried out in solution with potassium dichromate and dilute sulphuric acid, at such a temperature that the aldehyde distils off on formation, thus preventing further oxidation to the acid. This method is thus suitable for aldehydes of low boiling-point. Acetaldehyde is prepared in this way from ethyl alcohol :

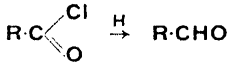
$$CH_3{\cdot}CH_2{\cdot}OH \xrightarrow{O} CH_3{\cdot}CHO$$

(2) By the dry distillation of a mixture in molecular proportions of the calcium or barium salt of the corresponding acid with calcium or barium formate :

$$(R{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca \rightarrow 2R{\cdot}CHO + 2CaCO_3$$

The reaction may be carried out under reduced pressure in a stream of an inert gas, to prevent oxidation and to carry off the aldehyde from the hot reaction mixture ; the method is only suitable for aldehydes which can be distilled without decomposition.

(3) By the catalytic reduction of the corresponding acid chloride :



$$R{\cdot}C\begin{matrix}\diagup Cl\\ \diagdown O\end{matrix} \xrightarrow{H} R{\cdot}CHO$$

This is generally carried out by passing hydrogen into a hot solution of the acid chloride in xylene containing a suspension of palladinised barium sulphate or kieselguhr, but for experimental details, *see* Rosenmund (Ber. 1918, **51**, 585) ; Rosenmund and Zetzsche (Ber. 1918, **51**, 594 ; 1921, **54** [B], 425) ; *also* Ber. 1921, **54** [B], 2888 ; 1922, **55** [B], 609.

(4) By hydrolysis of the dihalogen substitution product $R{\cdot}CHX_2$ by boiling with water or lime. Thus benzaldehyde may be prepared from benzal chloride :

$$C_6H_5{\cdot}CHCl_2 \xrightarrow{H_2O} C_6H_5{\cdot}CHO$$

The preparation can also be carried out with the monohalogen substitution product, by oxidation and hydrolysis with a suitable reagent. Benzaldehyde may be prepared from benzyl chloride by boiling with a solution of copper nitrate or other metallic nitrates :

$$C_6H_5{\cdot}CH_2Cl \xrightarrow{Cu(NO_3)_2} C_6H_5{\cdot}CHO$$

(5) By direct oxidation of a benzene homologue, thus pyrolusite and 60% sulphuric acid have been used for the preparation of benzaldehyde from toluene or chromyl chloride may be used as the oxidising agent (Étard's reaction).

(6) By treatment of the Grignard reagent with excess of ethyl formate or ethyl orthoformate, or disubstituted formamides :

$$R{\cdot}Mg{\cdot}X + H{\cdot}COOEt \rightarrow X{\cdot}Mg{\cdot}OEt + R{\cdot}CHO$$

$$\begin{aligned}R{\cdot}Mg{\cdot}X + CH(OEt)_3 &\rightarrow X{\cdot}Mg{\cdot}OEt + R{\cdot}CH(OEt)_2\\ &\qquad\qquad \downarrow H_2O\\ &\qquad\qquad R{\cdot}CHO\end{aligned}$$

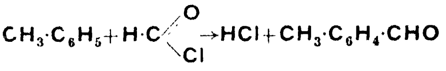
$$\begin{aligned}R''{\cdot}Mg{\cdot}X + H{\cdot}CONRR' &\rightarrow H{\cdot}CR''(OMgX)NRR'\\ &\qquad \downarrow H_2O\\ &\quad R''{\cdot}CHO + NHRR' + Mg(OH)X\end{aligned}$$

(7) From the corresponding nitrile by converting it to the imino chloride by means of stannous chloride in ether saturated with hydrogen chloride, the product is then hydrolysed by warm water to the aldehyde :

$$R{\cdot}CN \xrightarrow{HCl} R{\cdot}CCl : NH \xrightarrow{2H} R{\cdot}CH : NH,HCl \xrightarrow{H_2O} R{\cdot}CHO$$

(Stephen, J.C.S. 1925, **127**, 1874).

(8) From the aromatic hydrocarbon on treatment with carbon monoxide and hydrogen chloride, in the presence of aluminium chloride and cuprous chloride (Gattermann-Koch). (Unstable formyl chloride may be assumed to be the intermediate reagent.) The aldehyde group enters the para position to the alkyl group in the higher homologues of benzene :

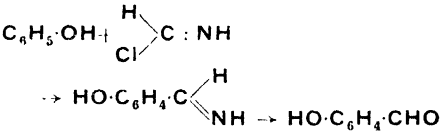


$$CH_3{\cdot}C_6H_5 + H{\cdot}C\begin{matrix}\diagup O\\ \diagdown Cl\end{matrix} \rightarrow HCl + CH_3{\cdot}C_6H_4{\cdot}CHO$$

See also Hey, J.C.S. 1935, 72.

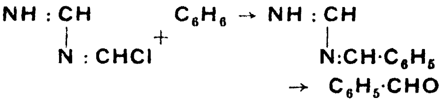
Iron pentacarbonyl has been used in place of carbon monoxide (Wolf, Ber. 1928, **61** [B], 1765).

(9) By treating phenols or their ethers with anhydrous hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride and subsequent hydrolysis. The aldehyde group enters the para position to the hydroxyl group :



$$C_6H_5{\cdot}OH + \begin{matrix}H\diagdown\\ Cl\diagup\end{matrix}C : NH \rightarrow HO{\cdot}C_6H_4{\cdot}C\begin{matrix}\diagup H\\ \diagdown NH\end{matrix} \rightarrow HO{\cdot}C_6H_4{\cdot}CHO$$

The work of Hinkel, Ayling, and Morgan (J.C.S. 1932, 2793) suggests that chloromethyleneformamidine and not the chloride of iminoformic acid is the active reagent, and shows that in the presence of excess of aluminium chloride and at a suitably high temperature the aldehyde can be thus prepared from the aromatic hydrocarbon itself :



$$\begin{matrix}NH : CH\\ |\\ N : CHCl\end{matrix} + C_6H_6 \rightarrow \begin{matrix}NH : CH\\ |\\ N{:}CH{\cdot}C_6H_5\end{matrix} \rightarrow C_6H_5{\cdot}CHO$$

By carrying out the experiment at 100° they obtained aldehydes from benzene, toluene, xylene and ethylbenzene, as well as from anisole and resorcinol.

The use of zinc cyanide in place of anhydrous hydrogen cyanide is suggested by Adams and Levine (J. Amer. Chem. Soc. 1923, **45**, 2373) and Adams and Montgomery (*ibid.* 1924, **46**, 1518).

(10) By treating a phenol with chloroform and sodium hydroxide (Reimer-Tiemann) :

$$C_6H_5{\cdot}OH \xrightarrow[NaOH]{CHCl_3} HO{\cdot}C_6H_4{\cdot}CHO$$

The aldehyde group enters chiefly the ortho position to the hydroxyl group ; some para compound is also formed. The ratio of the ortho to para compound formed is influenced by the metallic hydroxide used.

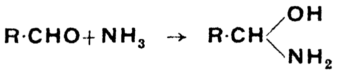
(11) By the catalytic dehydrogenation of alcohol (Sabatier and Senderens, Compt. rend. 1903, **136**, 738). Thus ethyl alcohol, passed over reduced copper heated to *circa* 250°, gives hydrogen and acetaldehyde :

$$CH_3{\cdot}CH_2{\cdot}OH \xrightarrow{Cu} CH_3{\cdot}CHO + H_2$$

At higher temperatures methane and carbon monoxide are also formed. *See also* Adkins, Kommes, Struss and Dasler for the use of copper-chromium oxide as catalyst (J. Amer. Chem. Soc. 1933, **55**, 2992).

Reactions (formation of additive and condensation compounds).—Aldehydes form a large number of addition compounds and condensation products, owing to the presence of the reactive carbonyl group.

(1) With ammonia :—Aliphatic aldehydes form aldehyde ammonias. These may be prepared by passing dry ammonia into a solution of the aldehyde in ether :

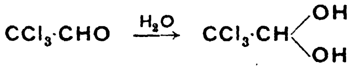


$$R{\cdot}CHO + NH_3 \rightarrow R{\cdot}CH\langle^{OH}_{NH_2}$$

These compounds give a useful method for the isolation and purification of aldehydes, as the free aldehyde may be regenerated by warming with dilute acid.

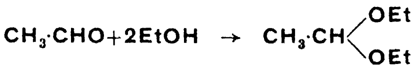
Formaldehyde and aromatic aldehydes do not give these compounds. Formaldehyde when treated with ammonia gives hexamethylenetetramine,$(CH_2)_6N_4$, and benzaldehyde and ammonia give *hydrobenzamide*, $(C_6H_5{\cdot}CH)_3N_2$.

(2) With water :—Aldehydes do not combine with water unless a negative radicle is associated with the carbonyl group ; thus chloral gives chloral hydrate :



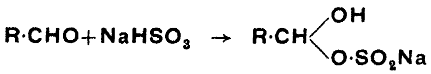
$$CCl_3{\cdot}CHO \xrightarrow{H_2O} CCl_3{\cdot}CH\langle^{OH}_{OH}$$

(3) With alcohol :—Acetals are formed on heating aldehydes and alcohols, or in the cold with a suitable catalyst such as a small quantity of hydrogen chloride :



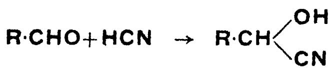
$$CH_3{\cdot}CHO + 2EtOH \rightarrow CH_3{\cdot}CH\langle^{OEt}_{OEt}$$

(4) With alkali bisulphites :—Aldehydes, on shaking with a saturated aqueous solution of sodium bisulphite, give bisulphite compounds which are usually crystalline. The latter may thus be used for the separation and purification of aldehydes, as the aldehyde is regenerated by treatment with dilute acid or alkali carbonate :



$$R{\cdot}CHO + NaHSO_3 \rightarrow R{\cdot}CH\langle^{OH}_{O{\cdot}SO_2Na}$$

(5) With hydrogen cyanide :—Cyanhydrins are formed by the addition of hydrogen cyanide to aldehydes :



$$R{\cdot}CHO + HCN \rightarrow R{\cdot}CH\langle^{OH}_{CN}$$

They are usually prepared by the action of potassium cyanide on the bisulphite compound On hydrolysis they give hydroxy acids :

$$R{\cdot}CH(OH)CN \rightarrow R{\cdot}CH(OH)COOH$$

(6) With hydroxylamine :—Aldehydes give oximes on treatment with hydroxylamine :

$$R{\cdot}CHO + H_2N{\cdot}OH \xrightarrow{NaOH} R{\cdot}CH : NONa \xrightarrow{CO_2} R{\cdot}CH : NOH$$

Oximes may usually be prepared by dissolving the required amount of hydroxylamine hydrochloride in a slight excess of dilute aqueous sodium hydroxide and adding the aldehyde, the oxime may be liberated from its sodium salt by passing carbon dioxide, and filtering if the oxime is insoluble in water, or if otherwise, extracting with ether.

(7) With semicarbazide :—Aldehydes give semicarbazones on treatment with semicarbazide :

$$R{\cdot}CHO + H_2N{\cdot}NH{\cdot}CO{\cdot}NH_2 \rightarrow R{\cdot}CH : N{\cdot}NH{\cdot}CO{\cdot}NH_2$$

Semicarbazide hydrochloride is dissolved in excess of a saturated aqueous solution of sodium acetate and the aldehyde added. If the latter is insoluble, alcohol may be added to bring it into solution. The mixture is well shaken and allowed to stand at room temperature.

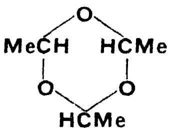
(8) With phenylhydrazine :—Aldehydes give phenylhydrazones on treatment with phenylhydrazine :

$$R{\cdot}CHO + H_2N{\cdot}NH{\cdot}C_6H_5 \rightarrow R{\cdot}CH : N{\cdot}NH{\cdot}C_6H_5$$

This condensation is usually carried out in dilute acetic acid solution.

Nitro and halogen substituted phenylhydrazones are usually less soluble and are more easily obtained crystalline than the phenylhydrazones, and thus afford useful derivatives for characterising the parent aldehyde.

(9) Aldehydes, especially the lower members, show a tendency to polymerise. Thus formaldehyde at ordinary temperatures gives trioxymethylene $(CH_2O)_3$, and acetaldehyde with a small amount of sulphuric or hydrochloric acid gives the internal ether, paraldehyde :



(10) Some aliphatic aldehydes undergo auto condensation (aldol condensation) under the influence of a number of reagents, by the linking of carbon to carbon. Thus acetaldehyde gives aldol :

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO \rightarrow CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$

If, however, the reagent is also a dehydrating agent, water is split off and an unsaturated aldehyde obtained. Crotonaldehyde is obtained in this way from acetaldehyde :

$$CH_3{\cdot}CHO + CH_3{\cdot}CHO \rightarrow CH_3{\cdot}CH : CH{\cdot}CHO + H_2O$$

(11) Aldehydes condense with certain alkyl aryl ketones in the presence of alkali giving unsaturated ketones :

$$\mathrm{R{\cdot}CHO + CH_3{\cdot}CO{\cdot}R' \rightarrow R{\cdot}CH : CH{\cdot}CO{\cdot}R' + H_2O}$$

Thus benzylideneacetone is prepared from benzaldehyde and acetone, and benzylidene acetophenone from benzaldehyde and acetophenone.

(12) Aromatic aldehydes condense with the sodium salts of aliphatic acids giving unsaturated acids. The condensing agent used is the anhydride of the fatty acid. Thus benzaldehyde and sodium acetate, on heating with acetic anhydride, give cinnamic acid :

$$\mathrm{R{\cdot}CHO + CH_3{\cdot}COOH \rightarrow R{\cdot}CH : CH{\cdot}COOH + H_2O}$$

(13) Aldehydes also condense with malonic acid and malonic ester :

$$\begin{aligned}&\mathrm{R{\cdot}CHO + CH_2(COOH)_2}\\ &\qquad\rightarrow \mathrm{R{\cdot}CH : C(COOH)_2}\\ &\qquad\quad\downarrow \text{heat}\\ &\qquad\quad \mathrm{R{\cdot}CH : CH{\cdot}COOH + CO_2}\end{aligned}$$

Benzalmalonic acid is formed in this way from benzaldehyde and malonic acid, in the presence of ammonia or aniline (*see also* Boehm, Arch. Pharm. 1929, **267**, 702 ; A. 1930, 88). This on heating loses carbon dioxide and is converted to cinnamic acid. Benzaldehyde and diethyl malonate give benzalmalonic ester,

$$\mathrm{C_6H_5{\cdot}CH : C(COOEt)_2}.$$

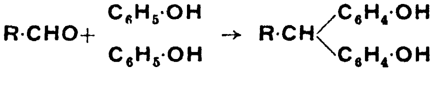
(14) Aromatic aldehydes on heating in alcoholic solution with potassium cyanide give the corresponding acyloin, thus benzaldehyde gives benzoin :

$$\mathrm{2Ph{\cdot}CHO \rightarrow Ph{\cdot}CH(OH){\cdot}CO{\cdot}Ph}$$

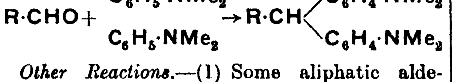
(15) Aromatic aldehydes condense with primary amines on warming, to give a Schiff base, *e.g.*

$$\mathrm{Ph{\cdot}CHO + H_2N{\cdot}Ph \rightarrow Ph{\cdot}CH : N{\cdot}Ph}$$

(16) Aromatic aldehydes condense readily with dimethylaniline and with phenols to give derivatives of triphenylmethane :



$$\mathrm{R{\cdot}CHO + \begin{matrix}C_6H_5{\cdot}OH\\ C_6H_5{\cdot}OH\end{matrix} \rightarrow R{\cdot}CH\Big\langle\begin{matrix}C_6H_4{\cdot}OH\\ C_6H_4{\cdot}OH\end{matrix}}$$



$$\mathrm{R{\cdot}CHO + \begin{matrix}C_6H_5{\cdot}NMe_2\\ C_6H_5{\cdot}NMe_2\end{matrix} \rightarrow R{\cdot}CH\Big\langle\begin{matrix}C_6H_4{\cdot}NMe_2\\ C_6H_4{\cdot}NMe_2\end{matrix}}$$

Other Reactions.—(1) Some aliphatic aldehydes and all aromatic aldehydes on treating with sodium hydroxide are converted into an equivalent mixture of the corresponding alcohol and acid (Cannizzaro's reaction) :

$$\mathrm{2R{\cdot}CHO + H_2O \rightarrow R{\cdot}CO{\cdot}OH + R{\cdot}CH_2{\cdot}OH}$$

Thus formaldehyde gives methyl alcohol and formic acid, benzaldehyde gives benzoic acid and benzyl alcohol, but acetaldehyde gives a yellow resin with a nauseous odour and this is a characteristic reaction of this aldehyde.

(2) Diazomethane reacts with aldehydes giving a methyl ketone :

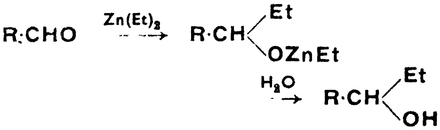
$$\mathrm{R{\cdot}CHO + CH_2N_2 \rightarrow R{\cdot}CO{\cdot}CH_3}$$

See also Arndt, Amende and Ender (Monatsh. 1932, **59**, 202) and Arndt, Eistert and Ender (Ber. 1929, **62** [B], 44).

(3) Phosphorus pentachloride reacts with aldehydes, the oxygen of the carbonyl group being replaced by two atoms of chlorine :

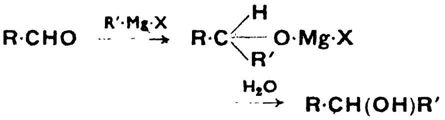
$$\mathrm{R{\cdot}CHO \xrightarrow{PCl_5} R{\cdot}CHCl_2}$$

(4) Zinc methyl and zinc ethyl form addition compounds with aldehydes, which give secondary alcohols when treated with water :



$$\mathrm{R{\cdot}CHO \xrightarrow{Zn(Et)_2} R{\cdot}CH\Big\langle\begin{matrix}Et\\ OZnEt\end{matrix} \xrightarrow{H_2O} R{\cdot}CH\Big\langle\begin{matrix}Et\\ OH\end{matrix}}$$

(5) Secondary alcohols are also obtained by treating with water the product of the reaction of a Grignard reagent and an aldehyde :



$$\mathrm{R{\cdot}CHO \xrightarrow{R'{\cdot}Mg{\cdot}X} R{\cdot}C\Big\langle\begin{matrix}H\\ O{\cdot}Mg{\cdot}X\\ R'\end{matrix} \xrightarrow{H_2O} R{\cdot}CH(OH)R'}$$

(6) Aromatic aldehydes may usually be directly nitrated or sulphonated.

(7) Aldehydes can be directly reduced to primary alcohols in the presence of heated nickel :

$$\mathrm{R{\cdot}CHO \xrightarrow{H_2} R{\cdot}CH_2{\cdot}OH}$$

or by sodium amalgam or other source of nascent hydrogen.

(8) The oxidation of many aldehydes by the air may be retarded by the addition of a small quantity of quinol. For the oxidation of aldehydes with selenium dioxide, *see* Riley, Morley, and Friend (J.C.S. 1932, 1875).

Detection and Identification.—(1) A solution of rosaniline hydrochloride, decolorised with sulphur dioxide (Schiff's reagent) gives a reddish-violet colour with aldehydes.

Some aromatic aldehydes react abnormally with Schiff's reagent and give yellow or red precipitates. This has been found to depend partly on the amount of free sulphur dioxide present in the reagent (Shoesmith, Sosson and Hetherington, J.C.S. 1927, 2221).

For the colour reactions of aldehydes with rosaniline hydrochloride in 98–100% formic acid, *see* Rumpf (Compt. rend. 1933, **197**, 337) ; and for the mechanism of the Schiff colour reaction for aldehydes, *see* Rumpf (Ann. Chim. 1935 [xi], **3**, 327, and Bull. Soc. chim. 1932 [iv], **51**, 503).

(2) Aliphatic aldehydes reduce Fehling's solution on warming, and cuprous oxide is precipitated.

(3) Aldehydes give a silver mirror when gently warmed with an ammoniacal silver nitrate solution.

(4) Oximes, semicarbazones, phenylhydrazones and substituted phenylhydrazones are much used for the detection and identification of aldehydes. Certain of these, *e.g.* the oximes, may exist in two forms (*cis* and *trans*), but usually one form is the more stable and can be obtained pure by crystallisation.

2 : 4-Dinitrophenylhydrazine has been shown to be a most useful reagent for aldehydes. A solution in 2*N*-hydrochloric acid is used for aldehydes soluble in water and a solution of the sulphate dissolved in alcohol for those insoluble in water. The dinitrophenylhydrazones are usually well-defined crystalline compounds with sharp melting-points. Brady and Elsmie (Analyst, 1926, 77) ; Allen (J. Amer. Chem. Soc. 1930, **52**, 2955) ; Brady (J.C.S. 1931, 756). For the preparation of the reagent from chloro-2 : 4-dinitrobenzene and hydrazine hydrate, *see* Brady, *l.c. See also* Ferrante and Bloom (Amer. J. Pharm. 1933, **105**, 381) ; Houghton (*ibid.* 1934, **106**, 62) ; Iddles and Jackson (Ind. Eng. Chem. (Anal.) 1934, **6**, 454), and Stain (J. Amer. Chem. Soc. 1935, **57**, 758). Reference may also be made to the following recent papers for reagents used for the identification of aldehydes : 3 : 5-dinitrobenzoylhydrazine (Sah and Ma, J. Chinese Chem. Soc. 1934, **2**, 40 ; A. 1934, 790) ; phenylsemicarbazide (Sah and Ma, *ibid.* 1934, **2**, 32 ; A. 1934, 791) ; *p*-nitrobenzhydrazide (Chen, *ibid.* 1935, **3**, 251 ; A. 1935, 1259) ; *o*-tolylsemicarbazide (Lei, Sah, and Shih, *ibid.* 1935, **3**, 246 ; A. 1935, 1259) ; *p*-tolylsemicarbazide (Sah and Lei, *ibid.* 1934, **2**, 167 ; A. 1934, 1016) ; 3-nitrobenzhydrazide (Meng and Sah, Sci. Rep. Nat. Tsing Hua Univ. 1934, **2**, 347 ; A. 1934, 1376) ; *o*-chlorobenzhydrazide (Sun and Sah, *ibid.* 1934, **2**, 359 ; A. 1934, 1376) ; *p*-chlorobenzhydrazide (Shih and Sah, *ibid.* 1934, **2**, 353 ; A. 1934, 1376) ; *β*-naphthylhydrazine (Lei, Sah, and Kao, *ibid.* 1934, **2**, 335 ; A. 1934, 1376) ; *o*-tolylhydrazine (Sah and Ma, *ibid.* 1932 ; A. **1**, 259 ; A. 1933, 498) ; *p*-tolylhydrazine (Sah and Lei, *ibid.* 1933, **2**, 1 ; A. 1933, 964) ; *p*-chlorophenylhydrazine (Sah, Lei, and Shen, *ibid.* 1933, **2**, 7 ; A. 1933, 964).

Estimation.—(1) By treating the aldehyde with a measured excess of hydroxylamine hydrochloride and titrating the liberated hydrochloric acid with standard alkali in the presence of a suitable indicator (Analyst, 1934, **59**, 105). Schultes (Angew. Chem. 1934, **47**, 258 ; A. 1934, 635) suggests the use of bromophenol blue in place of methyl orange as indicator in this method of estimation.

(2) Many aldehydes can be estimated by titrating with standard sulphuric acid a mixture of the aldehyde with excess of a *neutral* solution of sodium sulphite, using phenolphthalein as indicator. The reaction proceeds according to the equation :

$$2Na_2SO_3+2R{\cdot}CHO+H_2SO_4 \\ =2R{\cdot}CH(OH)SO_3Na+Na_2SO_4$$

The sodium bisulphite generated by the action of the acid on the normal sulphite combines with the aldehyde and, as this compound as well as the normal sulphite is neutral to phenolphthalein, the indicator shows no change until all the aldehyde has been converted into the bisulphite compound.

(3) Aldehydes may also be estimated by the addition of a measured excess of standard bisulphite solution to form the additive compound, and the determination of the excess of bisulphite with a standard solution of iodine.

(4) A method of estimating aromatic aldehydes given by Eck (Pharm. Weekblad, 1928, **65**, 68) is to dissolve in acetic acid and titrate with benzidine acetate solution.

(5) Micro methods for the estimation of semicarbazones are described by Hobson (J.C.S. 1929, 1384) and Veibel (J.C.S. 1929, 2423 ; Bull. Soc. chim. 1927, **41**, 1410). The former hydrolyses with a solution containing 15% hydrochloric acid and 5% mercuric chloride, the latter reagent oxidises the hydrazine as it is formed, and thus one-third of the nitrogen is obtained as ammonia, which is estimated by Pregl's micro Kjeldahl method ; the latter hydrolyses with sulphuric acid and uses iodic acid as oxidising agent :

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2+H_2O \\ \rightarrow NH_3+CO_2+NH_2{\cdot}NH_2$$

$$NH_2{\cdot}NH_2+2HgCl_2 \\ \rightarrow N_2+2Hg+4HCl$$

(6) Aldehydes may be estimated by the addition of excess of phenylhydrazine to form the phenylhydrazone, and the determination of the excess of phenylhydrazine—*see* Watson, Smith, and Kaufler (Chem. News, 1906, **93**, 83) ; Smedley MacLean (Biochem. J. 1913, **7**, 611). A modification of this method is due to Ellis (J.C.S. 1927, 848). They may also be estimated by the precipitation and weighing of the phenylhydrazone (or substituted phenylhydrazone). The use of 2 : 4-dinitrophenylhydrazine for this purpose is described by Iddles and Jackson, *l.c.*, and by Houghton, *l.c.* J. N. E. D.

ALDEHYDINES. The name given by Ladenburg (Ber. 1877, **10**, 1126 ; 1878, **11**, 1648, 1656) to the *N*-alkyl benziminazoles formed by the condensation of ortho-diamines with aldehydes (*v.* AMINES).

The name *aldehydine* is also given to the *collidine*, *a*-methyl-*β′*-ethylpyridine, b.p. 178°, which is prepared by heating aldehyde-ammonia in alcoholic solution.

ALDER BARK. The bark of the common or black alder, *Alnus glutinosa* (Fam. Betulaceæ), has been used for tanning and dyeing, and the wood for pulp. Differing values are recorded for the percentage of tannin: 5–9% (1% in old trees)—Smaic and Wladika (Collegium, 1921, 250); B. Hunt (J.S.C.I. 1885, **4**, 264). In the earlier literature up to 20% is recorded. The tannin resembles oak tannin. The extract has been used for dyeing linen and for colouring skins ; for the dyes obtainable from the bark *v.* N. Filippow (J.S.C.I. 1925, **44**, 348). J. Zellner (Monatsh. 1926, **46**, 309 ; A. 1926, 646) isolated *protalnulin* and *alnulin* from this bark. M. Bridel and C. Charaux (Compt. rend. 1930, **191**, 1151 ; A. 1931, 131) obtained franguloside (frangulin) and frangularoside (*ibid.*, *idem*, 1374, A. 1931, 274). From grey alder bark, *Alnus incana*, J. Zellner *et al*

(Monatsh. 1930, **56**, 204 ; A. 1930, 1627 ; *cf. ibid.* 1924, **44**, 261 ; A. 1924, **1**, 814) prepared alniresinol, alnulin, and protalnulin. For green alder bark, *A. viridis*, *v.* J. Zellner (*ibid.* 1926, **47**, 151 ; A. 1926, 1281). The bark of the red alder, *A. rubra*, is not a remunerative source of tannin (R. H. Clark and H. R. Offord, Trans. Roy. Soc. Canada, 1926 [iii], **20**, III, 149 ; B. 1926, 683). Symbiotic fixation of nitrogen in the root nodules of alders is responsible for the whole of their nitrogen nutrition (M. Roberg, Ber. Deut. bot. Ges. 1934, **52**, 54 ; A. 1934, 417). J. N. G.

ALDER BUCKTHORN BARK. Frangula bark, *Rhamnus frangula* (Fam. Rhamnaceæ), a European shrub. The bark contains frangulin 2·5% (M. Bridel and C. Charaux, Bull. Soc. chim. biol. 1933, **15**, 642 ; A. 1933, 877). In medicine the bark may be used instead of cascara sagrada.

ALDOL, β-hydroxybutaldehyde, *v.* ACETALDEHYDE, (v), *c.*

The formation of aldol from acetaldehyde is an example of the *aldol condensation* which also occurs between two different aldehydes, two ketones, or an aldehyde and a ketone, the necessary condition being that in at least one of the reactants the carbon atom adjacent to the carbonyl group shall be united to a hydrogen atom, *e.g.* :

$$R_3C{\cdot}CHO+R_2CH{\cdot}CHO = R_3C{\cdot}CH(OH){\cdot}CR_2{\cdot}CHO$$

The aldols as a class are colourless liquids, of general properties similar to those of aldol itself.

ALDREY *v.* ALLOYS, LIGHT.

ALDUR. (Trade name.) A urea-formaldehyde moulding powder. *See* article on UREA-FORMALDEHYDE PLASTICS.

ALDURAL *v.* ALLOYS, LIGHT.

ALETODIN *v.* ASPIRIN.

ALEUDRIN. Trade name for αα-dichloro*iso*propyl carbamate.

ALEURITES SPECIES (Fam. Euphorbiaceæ). Tropical trees bearing fruit enclosing a hard kernel (nut) within which are seeds containing about 50% of oil. Two species supply Tung oil or China wood oil much used in varnishes or enamels (*cf.* R. S. Morrell, "Varnishes and their Components," 1923). *A. cordata*, growing in Japan, yields Japanese wood oil, decidedly inferior to China wood oil, but forming a firm gel. *A. Fordii*, wild and cultivated in South China, supplies about 90% of China wood oil ; the remainder is derived from *A. Montana*. The nuts are separated by hand from the soft tissue, either after roasting the fruit until it bursts or after allowing stacks of the fruit to ferment. The nuts are ground under stone rollers driven by buffaloes, the meal is then roasted lightly, steamed in baskets placed above cauldrons, drained and the oil expressed in primitive wooden presses. The characteristic constituent is the glyceride of α-elæostearic acid. When heated to 280°–300°, the oil sets in a few minutes to a firm jelly ; under defined conditions this property becomes an important test (*cf.* B.S.I. Specification No. 391, 1936). The Chinese prepare a varnish for junks by heating the oil for an hour ; it is also burnt for its soot used in making China ink. The oil is shipped to Europe and America from Hankow. The oil has often been adulterated, while the crude method of manufacture causes variations in quality. This uncertain quality and the value of the oil about £16 per ton above the price of linseed oil, caused the establishment of plantations of *A. Fordii* and to a smaller extent of *A. Montana* in the Empire, the United States, Algeria, and elsewhere (Bull. Imp. Inst. 1932, **30**, 24, 271 [B. 1933, 75] ; 1933, **31**, 327 ; 1934, **32**, 560 ; 1935, **33**, 353). Since January, 1930, the Paint and Varnish Research Association have carried out investigations in connection with the plans for Empire development co-ordinated by the Tung Oil Committee of the Imperial Institute (L. A. Jordan, J.S.C.I. 1934, **53**, 1T; B. 1934, 208—experimental study of specifications). *A. Moluccana* yields lumbang oil used in the Philippines for paint and soft soap manufacture. *A. Montana* provides about 10% of the output of China wood oil; has analytical constants inferior to the oil from *A. Fordii* (*cf.* Jordan, *l.c.*, and Bull. Imp. Inst. 1930, **28**, 267 ; B. 1931, 30). *A. triloba* supplies candlenut oil used as a burning oil in Fiji, the West Indies and Brazil. J. N. G.

ALEURONE GRAINS. Granular deposits occurring in cells of many plant seeds, usually towards the external surface. The grains exhibit a more or less regular shape resembling crystals. Actually they consist of an amorphous protein matrix in which is embedded the "crystalloid" protein and a globoid body composed principally of a double phosphate of calcium and magnesium. The whole is usually surrounded by an outer protein layer which is less easily soluble than the internal contents. The term "crystalloid" in botanical nomenclature must be regarded as merely descriptive of the appearance. Treatment with dilute acid or alkali causes the "crystalloid" to swell up in a manner characteristic of colloidal protein matter. Moreover, the "crystalloid" does not diffuse through a membrane.

The proteins contain one, possibly two, globulins and an albumin. Posternak (Compt. rend. 1905, **140**, 322) detected phytin in aleurone material and records the following analysis of grains from (i) spruce fir, (ii) sunflower, (iii) hemp, (iv) white lupin.

	(i)	(ii)	(iii)	(iv)
N	12·97	10·22	12·88	10·70
K	2·50	2·20	2·71	—
Ca	0·37	0·33	0·27	0·11
Mg	1·25	1·46	1·67	0·28
Fe	0·09	0·05	0·05	—
Mn	0·25	trace	trace	0·11
P	2·67	2·78	3·83	0·61
S	0·64	0·64	0·81	—
Si	0·35	0·24	0·36	0·01

In no case was sodium or chlorine detected. In cereals and many grass seeds the outer layer of the endosperm consists of short, prismatic, thin-walled cells containing aleurone grains—the aleurone layer. Some doubt exists as to the exact function of this layer in the seeds. The earlier view that enzymes bringing about the biochemical changes in seeds during germination were excreted by the aleurone layer seems somewhat discredited by more recent work (Mann and Harlan, U.S. Dept. Agric. Bull. 1915, No. 183). Enzyme excretion is now regarded as the function of the epithelial layer, the aleurone layer acting as a protective. The nitrogenous matter of the aleurone does not appear to act as a reserve food for the growing embryo in the early stages but is probably utilised by the young leaved seedling when it has the power of manufacturing its own carbohydrate material. A. G. Po.

ALEXIPON. Trade name for ethyl salicylate, $C_6H_4(OH)COOC_2H_5$. Antirheumatic.

ALFA. *Alva. Halva.* Arabic name for esparto grass, especially Algerian esparto.

ALFALFA. An Arabic word "the best fodder," applied in America to the plant *Medicago sativa* (Fam. Leguminoseæ), known in England as lucerne.

ALGÆ. (*Varech* or *Algues*, Fr.; *Algen*, Ger.) A widely distributed class of plant life belonging to the lowest division (Thallophyta) and comprising many salt and fresh water forms, diatoms and vegetable plankton; members of this group are also found on or in the soil, on rocks and on tree trunks.

Iodine was discovered by Curtois in 1812 in the mother liquor of *kelp*, the ash of burnt seaweed, and the kelp from certain seaweeds is still a source of iodine of industrial importance. Owing to the high percentages of sugar-like materials, several algæ have occasionally been used as foodstuffs, *e.g.* dulse (*Rhodymenia palmata*) and murlins (*Alaria esculenta*). The mucilaginous nature of many marine algæ has led to their use for the production of gums and size substitutes, the principal alga employed being carragheen or, as it is more commonly known, Irish moss (*Chondrus crispus*). The production of agar-agar from algæ of the *Gelidium* species is an important industry (*see* AGAR-AGAR). Use has also been made of marine algæ for the production of acetic acid by destructive distillation, but this process, as also the production of alcohol by fermentation, is of minor importance.

Only the main algal species have been examined with regard to their chemical components and of these only the red and brown marine groups have received other than scant attention.

PHÆOPHYCEÆ (brown algæ). *Fucoxanthin*, the typical carotenoid pigment of this class and the subject of considerable research, was first detected by Millardet in 1869 and isolated in the crystalline state by Willstätter and Page (Annalen, 1914, **404**, 237). In 1935 Heilbron and Phipers (Biochem. J. 1935, **29**, 1369) reinvestigated the problem and showed that on the death of the plant (in this case the bladder wrack, *Fucus vesiculosus*), fucoxanthin (*see* FUCOXANTHIN) passes into zeaxanthin, a finding explaining many incompatible results hitherto reported. These authors showed that the only other lipochrome present was the hydrocarbon β-carotene. Willstätter and Page (*l.c.*) stated that the chlorophyll of the *Phæophyceæ* is mainly chlorophyll-*a*, chlorophyll-*b* being only present to about 5%. This somewhat contradicts the earlier work of Stokes (Proc. Roy. Soc. 1864, **13**, 144), who stated that the yellowish-green chlorophyll (chlorophyll-*b*) was present in relatively large amounts. The nature of the other pigment, phycophain, has not as yet been elucidated. *Phycophain*, a brown, water-soluble pigment, exists only in the dead plant and, according to Kylin (Z. physiol. Chem. 1912, **82**, 221), is produced by an alkaline reaction of the extraction liquors promoting oxidation of a colourless substance, *fucosan* (*see later*).

Comparatively little is known of the nature of the fatty food reserves of the phæophyceæ. Haas and Hill (Ann. Bot. 1933, **47**, 55; *cf. also* Russell-Wells, Nature, 1932, **129**, 654) observed that the amount of fat decreased with increasing depth and that the percentage of unsaponifiable material increased with increasing depth. Takahashi, Shirahama and Tase (J. Chem. Soc. Japan, 1933, **54**, 619) have identified caproic, caprylic, capric, myristic and linoleic acids in the fats.

Heilbron, Phipers, and Wright (J.C.S. 1934, 1572) have examined the bladder wrack (*Fucus vesiculosus*) and observed that the sterol present, named by them *fucosterol*, was a hitherto unknown member of the sterol group (*see* FUCOSTEROL), and that the paraffin hydrocarbon, hentriacontane, $C_{31}H_{64}$, a common constituent of leaf waxes, was also present, together with a considerable amount of terpenoid material, which so far has not been further examined. *Lactoflavin* (*see* FLAVINS), apparently present in all living matter, was isolated from *Fucus vesiculosus* by Heilbron, Parry and Phipers (Biochem. J. 1935, **29**, 1382) in the form of the photoderivative, *lumilactoflavin*.

One of the earliest algal carbohydrates to receive attention was *laminarin*, isolated in 1885 by Schmiedeberg from various members of the *Laminaria* (a subgroup of the *Phæophyceæ*). Laminarin gives no colour with iodine and is hydrolysed but slowly with vegetable diastase. It has been defined by Colin and Ricard (Compt. rend. 1929, **188**, 1449; Bull. Soc. chim. biol. 1930, **12**, 88), who used *Laminaria flexicaulis* as the source. These authors have shown that laminarin possesses the formula $(C_6H_{10}O_5)_6$ or $_7$, is dextrorotatory and yields only glucose on hydrolysis. Kylin (Z. physiol. Chem. 1913, **85**, 171; 1915, **94**, 371) found reducing sugars in almost insignificant quantities (0·01–0·2% of the dry weight) in the *Fucaceæ* (a subgroup of the *Phæophyceæ*), but whilst in *Ascophyllum nodosum* and *Fucus vesiculosus* the sugars are lævorotatory, in the *Laminaria* they are dextrorotatory. The hexol, mannitol (mannite), was isolated in 1844 by Stenhouse (J.C.S. 1844, **2**, 136) from *Ascophyllum nodosum*, this finding being confirmed by Kylin (Z. physiol. Chem. 1915, **94**, 371) and Haas and Hill (Ann. Bot. 1933, **47**, 55), who have shown that it is present in all *Phæophyceæ*.

With regard to the cell wall constituents Stanford (Chem. News, 1883, **47**, 254) extracted a very slimy substance, algin, from the *Laminaria* with sodium carbonate. Kylin (Z. physiol.

Chem. 1913, **85**, 171) showed that this material consists of three substances, algin, fucin and fucoidin. Nelson and Cretcher (J. Amer. Chem. Soc. 1929, **51**, 1914) showed that the hydrolytic products of algin (the calcium salt of a true acid, alginic acid), were uronic acids, the final product being *d*-mannosaccharic dilactone, (*see* Alginic Acid). Fucin was shown to be similar to algin (Kylin, Z. physiol. Chem. 1913, **85**, 171), the only noteworthy difference being that it gives a blue colour with iodine, potassium iodide and sulphuric acid, whilst algin does not. Bird and Haas (Biochem. J. 1931, **25**, 403) have shown that fucoidin is the calcium salt of a sulphuric ester of a non-reducing polymerised uronic acid combined with a methylpentosan.

Mention has been made of the water-soluble pigment phycophain and of its production by alkaline oxidation of a colourless substance, fucosan. This latter compound was first defined by Kylin (Z. physiol. Chem. 1913, **85**, 171) who showed that it was a tannin-like substance even though it gives no tannin reaction with ferric chloride and no sugar is formed on hydrolysis. If, therefore, fucosan be a member of the polysaccharide series, it is one of a hitherto unknown type. Fucosan gives precipitates with aqueous solutions of inorganic salts, *e.g.* lead acetate, silver nitrate, etc. ; and in aqueous acid solution it coagulates gelatin. The chemistry of this substance has been neglected and no further work appears to have been done on it, although it is obviously one that possesses remarkable properties. Kylin considered that it was one of the primary products of assimilation of the *Fucaceæ*, being formed in an analogous manner to laminarin. This view is supported by the fact that certain brown algæ such as *Fucus vesiculosus* and *Halidrys siliquosa* contain fucosan and no laminarin whilst others such as the *Laminaria* contain laminarin but no fucosan.

Rhodophyceæ (red algæ). The principal pigments in this class are non-carotenoid in character and are of the chlorophyll type. In 1892 Nadson, working on these red and blue algæ (it should be noted that many freshwater *Rhodophyceæ* are blue in colour) isolated a water-soluble pigment which he named hydrochrome. Further investigations by Kylin (Z. physiol. Chem. 1910, **69**, 169) showed that there were at least two of these pigments and, noting their albuminoid character, he renamed these pigments the chromoproteins. The name ***phycoerythrin*** was recalled from the early work of Kutzing (Phycologia generalis, 1843, 20) for the red chromoprotein and the blue analogue was designated ***phycocyan***. Phycoerythrin, recently isolated by Lemberg (Annalen, 1928, **461**, 46 ; 1930, **477**, 196 ; 1933, **505**, 151) and Kitasato (Acta Phytochim. 1925, **2**, 75) from *Ceramium rubrum*, forms hexagonal plates, yielding carmine red solutions tending towards a violet shade on concentration ; according to Lemberg, the aqueous solutions show absorption maxima at 565, 540 and 495$m\mu$. Phycocyan, also isolated from *Ceramium rubrum*, forms rhombohedral plates and yields bright blue solutions tending towards a violet red on concentration; the absorption maxima in aqueous solution are situated at 615 and 550$m\mu$. The chromoproteins themselves are highly complex, but Lemberg showed that digestion of the pigment solutions with pepsin hydrochloride splits the molecules into protein and chromogenic fractions (*see* Bile Pigments). The amphoteric pigmented portions, which he named ***phycoerythrobilin*** and ***phycocyanobilin*** respectively, are closely related to the bile pigments, *e.g.* phycocyanobilin has a similar absorption spectra to that of bilicyanin produced from bilirubin ; and phycoerythrobilin shows a corresponding resemblance to urobilin. Kylin (Z. physiol. Chem. 1911, **74**, 272) and Marchlewski (Z. physiol. Chem. 1911, **75**, 272) have shown that where chlorophyll-*b* does occur in the *Rhodophyceæ*, it is only in traces, the main green pigment being chlorophyll-*a*. Nothing definite was known of the lipochromes, until 1935, when Heilbron, Parry and Phipers (Biochem. J. 1935, **29**, 1376) showed that the red alga, *Rhodymenia palmata* contains β-carotene, taraxanthin and lutein (*see* Carotenoids) and that like the *Phæophyceæ* it contains the algal sterol, fucosterol, and the hydrocarbon, hentriacontane. In this connection the authors made some interesting observations, which are dealt with at the end of this article.

The characteristic polysaccharide of the *Rhodophyceæ* as yet has not been identified. According to Takahashi (J. Chem. Soc. Japan, 1919, **40**, 157) it yields a new sugar, *floridose*, which resembles galactose but fails to furnish mucic or saccharic acids on oxidation. Floridose crystallises from water in prisms, has m.p. 152°–153° and $[\alpha]_D$ +80·75°. (hydrazone, m.p. 156°–158°). It is apparently an aldohexose (reducing to a hexol, *floriditol*, prisms from water, m.p. 186°–187°) as it does not respond to tests for pentoses, ketoses or methylpentoses. Manganot (Compt. rend. Soc. Biol. 1921, **84**, 406) assumes that the unknown parent carbohydrate (" Floridean starch "), which gives a reddish-violet coloration with iodine, is related to glycogen. Kylin (Z. physiol. Chem. 1913, **85**, 171 ; 1915, **94**, 371) found no reducing sugars in the *Florideæ* (a subgroup of the *Rhodophyceæ*), but stated that one of the latter, *Rhodymenia palmata*, contained trehalose, a statement which was shown to be incorrect by Colin and Guéguen (Compt. rend. 1930, **190**, 653), who found that galactose was one of the hydrolytic products of the sugar. *Rhodymenia palmata* and *Corallina officinalis* were shown by Colin and Guéguen (Compt. rend. 1931, **191**, 63), and by Haas and Hill (Biochem. J. 1933, **27**, 1802) to contain *floridoside*, which is a monogalactoside of glycerol, the sugar being attached to the secondary hydroxyl grouping. Floridoside crystallises from alcohol, has m.p. 126°–127°, and $[\alpha]_D$ +158·4° (hexa-acetyl derivative : prisms from a mixture of alcohol and light petroleum, m.p. 100°–101°, $[\alpha]_D$ +108·5°). The same alga was observed by Sauvageau and Denigès (Compt. rend. 1922, **174**, 791) to effloresce a xylan. Takahashi (*l.c.*) could find no alginic acid in the *Florideæ*.

Chlorophyceæ (green algæ). Despite their abundance little is known of the composition of the green algæ. From the sea lettuce (*Ulva* *lactuca*) Willstätter and Page (*l.c.*) isolated the two chlorophylls in the proportions *a* : *b* : 4 : 3, xanthophyll and carotene, and it was generally assumed that the *Chlorophyceæ* were in this respect identical with the higher plants. Recently, however, Heilbron, Parry and Phipers (Biochem. J. 1935, **29**, 1376) have shown, as illustrated in the following table, that there is a specific difference in the unsaponifiable constituents of these two classes.

			Lipochromes					Sterols	
		Hentriacontane	β-Carotene	α-Carotene	Lutein	Taraxanthin	Fucoxanthin	Sitosterol	Fucosterol
	Land plants	+	+	+	+	+	—	+	—
Chlorophyceæ	*Œdogonium*	+	+	+	+	+	—	+	—
	Cladophora sauteri	+	+		+	+	—	+	+
	Nitella opaca	+	+	—	+	+	—	+	+
Rhodophyceæ	*Rhodymenia palmata*	+	+	—	+	+	—	—	+
Phæophyceæ	*Pelvetia canaliculata*	+	+	—	—		+	—	+
	Fucus vesiculosus	+	+	—	—	—	+	—	+
	Laminaria digitata	+	+	—	—	—	+	—	+

It will be observed that the *Chlorophyceæ* (with the exception of the *Œdogonium*) contain both the algal sterol, fucosterol and the typical phytosterol, sitosterol. In the *Rhodophyceæ* sitosterol is absent, only fucosterol being present; although this group does not contain the sterol of the land plants, it still retains the typical phytoxanthophylls, viz. taraxanthin and lutein. In the *Phæophyceæ* even this last relationship to the land plants is severed, the characteristic pigment fucoxanthin being substituted. *Œdogonium*, which presents an absolute parallel to the land plant (containing no fucosterol) and apparently an exception to the rule, however, shows but few points of botanical affinity with the other *Chlorophyceæ*. From the green algæ *Cladophora sauteri* Heilbron, Parry and Phipers, (Biochem. J. 1935, **29**, 1382) isolated lactoflavin as its tetra-acetyl derivative.

The other algal species have, from time to time, received attention but no fundamental knowledge has been brought to light apart from the fact that the blue-green algæ (*Cyanophyceæ*) contain chromoprotein pigments.

Certain algæ are characteristic of water containing sewage and some play an important rôle in the disinfection of polluted rivers. In storage reservoirs some of the algal growths (*e.g. Dinobryon* or *Tabellaria*) give rise to taste troubles, others (*e.g. Asterionella* and *Fragilaria*) exercise a serious blocking or choking effect on filtration processes. Copper sulphate (1–10 lb. per 1,000,000 gallons) has proved to be a valuable algicidal agent. I. M. H. and R. F. P.

ALGAROBILLA. *Algaroba.* The pods of *Cæsalpina brevifolia* (Fam. Leguminosæ) exported from Chili are used in tanning. They contain 35–52% of tannins including free and combined ellagic acid. The extract, which is mostly used as an addition to other tanning liquors to brighten the colour of the leather, is unstable and if kept imparts a dark brown colour.

ALGAROTH, POWDER OF. *Pulvis Algarothi, English Powder.* A crystalline oxychloride of antimony (*v.* ANTIMONY).

ALGARROBIN. A natural dye product obtained from the wood of the carob tree, *Ceratonia siliqua*, found in the Argentine. According to a report of the United States Consul-General at Buenos Ayres, it is largely employed in the Argentine for dyeing khaki cloth for military purposes, and some quantity is also imported to the continent of Europe. It is said to dye the textile fibres a light brown colour, though if these be previously mordanted more varied shades may be obtained. As it acts also as a mordant for the coal tar colours, it would appear to be a tannin, and may be allied to ellagitannin, the chief constituent of algarobilla (*see* ALGAROBILLA, *supra*).

A. G. P. and E. J. C.

ALGIN *v.* ALGINIC ACID.

ALGINASE. An enzyme present in aqueous extracts of the intestines of *Haliotus giganteus*, hydrolyses alginic acid, Oshima (J. Agric. Chem. Soc. Japan, 1931, 7, 328).

ALGINIC ACID. **Algin.** (*See also* ALGÆ.) Stanford (Chem. News, 1883, **47**, 254) extracted a mucilaginous substance from the bladder wrack (*Fucus vesiculosus*) with aqueous sodium carbonate, which he named algin. Kylin (Z. physiol. Chem. 1915, **94**, 337) showed that Stanford's algin consisted of algin, fucin and fucoidin and he stated that algin was the calcium salt of a true acid, alginic acid.

Commercial algin or sodium alginate resembles gum arabic and, in the sheet form, can scarcely be distinguished from gelatin, from which it differs by the solution not gelatinising, and by giving no reaction with tannin. It is distinguished from albumen by not coagulating on heating; from starch by giving no colour with iodine; from dextrin and gum arabic by its insolubility in dilute acids. All mineral acids and citric, tartaric, lactic, oxalic and picric amongst the organic acids, precipitate alginic acid in a gelatinous form and a 2% solution becomes semi-solid when thus treated. In this respect it resembles a strong solution of egg albumen, and it can be employed for thickening colours in printing or as a mordant in the same manner.

A solution of algin precipitates all the alkaline earths as alginates, with the exception of magnesium, the alginate of which is soluble. It precipitates nearly all the heavy metals as alginates, but gives no precipitate with mercuric chloride, or with potassium silicate.

In addition to sodium alginate, potassium, ammonium, lithium and magnesium alginate are all soluble algins, and scarcely distinguishable in appearance. The solution of algin resembles that of gum arabic, which in many of its applications it may be expected to replace ; it is quite soluble in cold water, but the solution takes about 12 hours to complete. It is so extremely viscous that a 2% solution is as thick as a 50% solution of gum arabic, and a 5% solution is poured with difficulty out of a wide-mouthed bottle. Alginic acid is insoluble in water, so that in dressing fabrics the soluble algin forms a flexible varnish, which can be converted into a lustrous hard glaze by passing it through a weak mineral acid. This process, which would destroy the ordinary starch and gum dressings, renders it also permanent and insoluble in water, the fabric becoming waterproof. As the alginates of calcium, aluminium, iron, etc., are all insoluble, the same effect is obtained by the use of solutions of these metals for the final wash. Alginic acid when dry resembles albumen, but it can be obtained also in thin transparent sheets, and readily coloured like gelatin, from which, however, it differs in being insoluble in hot water. It can also be obtained in blocks. Calcium alginate resembles it, but is whiter, like bone.

Aluminium alginate is very soluble in ammonia, and the aluminium ammonio-alginate is insoluble when dry, so that it makes a cheap waterproof varnish. It forms a good mordant or dung substitute in dyeing. Copper alginate is soluble in ammonia, forming a beautiful blue copper ammonio-alginate, which is also insoluble when dry, and makes a varnish useful for waterproofing fabrics which are liable to decomposition or to the attack of insects.

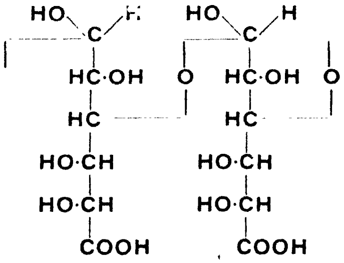
Ferric alginate is also soluble in ammonia, forming a bright red ferri-ammonio-alginate ; insoluble when dry, and proposed as a styptic, and for administering iron internally.

Nickel, cobalt, zinc, cadmium, manganese, chromium, uranium, silver, platinum, tin, arsenic and antimony all form soluble ammonio-alginates, some of which are beautiful salts. Sodium alginate, mixed with a dichromate, is sensitive to light in the same way as gelatin, the mixture becoming insoluble in water after exposure to light.

Hoagland and Lieb (J. Biol. Chem. 1915, **23**, 287) obtained alginic acid from *Macrocystis pyrifera* by treating a sodium carbonate extract with hydrochloric acid, and purified it by reprecipitating the acid from the sodium salt and, finally, reprecipitating the acid several times from the sodium salt which had been purified by dialysis. They proposed a formula $C_{21}H_{27}O_{20}$ and gave the optical activity as $[\alpha]_D - 169{\cdot}2°$ in aqueous solution and the neutralisation value as 325. The sugar produced on hydrolysis, according to these authors, closely resembled xylose. Atsuki and Tomoda (J. Soc. Chem. Ind. Japan, 1926, **29**, 599) suggested that alginic acid contained a uronic acid, as they found that 20% of the weight was lost as carbon dioxide by boiling with hydrochloric acid. This suggestion was supported by Schmidt and Vocke (Ber. 1926, **59** [B], 1585), who claimed that hydrolytic experiments indicated that alginic acid was a polymerised glycuronic acid.

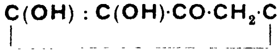
Nelson and Cretcher (J. Amer. Chem. Soc. 1929, **51**, 1914) isolated pure alginic acid from *Macrocystis pyrifera* and found that the optical activity of the sodium salt was $[\alpha]_D^{20} - 133°$. They observed that its most striking property was the power of adsorption of water and salts : dried at 100° it will adsorb 200–300 times its weight of water whereas it is itself insoluble in this solvent. Alginic acid does not reduce Fehling's solution but forms reducing substances if dried at 100°. Because of this sensitivity, alginic acid varies in rotation and acid value according to the time of drying. It liberates carbon dioxide from carbonates and can be titrated to a definite end-point, using phenolphthalein. Nelson and Cretcher stated that hydrolysis indicated that alginic acid is "a polymer of the anhydride of an aldehyde sugar acid in which all the aldehyde groups are conjugated and all the carboxyl groups free." The mannuronic acid, which was not isolated, can be oxidised to *d*-mannosaccharic dilactone (*cf. also* Bird and Haas, Biochem. J. 1931, **25**, 403, who independently obtained identical results).

Miwa (J. Chem. Soc. Japan, 1930, **51**, 738 ; Sci. Rep. Bunrika Daigaku, 1932, **2**, 23) isolated the mannuronic acid as the cinchonine or brucine salt and suggested a lactonic structure for alginic acid, $C_{24}H_{30}O_{23}$. Dillon and McGuinness (Sci. Proc. Roy. Dublin Soc. 1931, **20**, 129) gave the formula as $(C_6H_8O_6)_n$ and decided that when dry, alginic acid is lactonic. They advanced the structural formula I.



I.

Gomez (Amer. Chem. Abstr. 1934, **28**, 2701) states that alginic acid softens at 180° and carbonises at 250°–300°, that the neutralisation number is 194, and he showed that sodium alginate has $[\alpha]_D - 132°$. Gomez advanced the formula $(C_6H_{10}O_7)_n$ where $n = 4$ or a multiple thereof, alginic acid possessing one replaceable hydrogen atom per unit. He found that when treated with hot mineral acids alginic acid yielded carbon dioxide and furfural and obtained no evidence of the presence of free aldehyde groups ; acid hydrolysis yielded *d*-mannuronic acid in amounts indicating that alginic acid is a polymer of this acid. Ugami (Amer. Chem. Abstr. 1934, **28**, 7259) obtained a product $C_5H_6O_3$ on hydrolysis which was shown to be ***reductic acid*** (II) (Reichstein and Oppenauer, Helv. Chim. Acta, 1934, **16**, 390).



$$C(OH):C(OH){\cdot}CO{\cdot}CH_2{\cdot}CH_2$$

II.

Colin and Ricard (Bull. Soc. chim. biol. 1931, **13**, 417) investigated the occurrence of alginic acid in various algæ and found that the maximum amount occurs at the time of sporulation. Oshima (Amer. Chem. Abstr. 1931, **25**, 5681) discovered that alginic acid can be hydrolysed by alginase, an enzyme present in aqueous extracts of the intestines of *Haliotus giganteus*.

Commercially alginic acid is used in the explosives industry as a stabilising and "deadening" medium and also as a thickening agent in alkaline dyeing. Tests show that it is a good dispersing agent in the water dispersion of rubber and it has been successfully used as such in the rubbering of textiles (Kolesow, Amer. Chem. Abstr. 1933, **27**, 6014).

I. M. H. and R. F. P.

ALGIRON (*Alginoid iron*). Trade name for an iron compound of alginic acid (from seaweed); contains 11% iron.

ALGODONITE. A copper arsenide of a steel-grey colour. Found in the Lake Superior copper-mining district.

ALGOL BLUES, Bordeaux 3 B, Red BTK, Pink R, Scarlet G, Yellow GC, *v.* ANTHRAQUINONE DYESTUFFS.

ALGOL COLOURS *v.* ALIZARIN AND ALLIED DYESTUFFS; VAT DYES.

ALIVAL. Trade name for $\alpha\beta$-dihydroxy-γ-iodopropane, m.p. 48°–49°; also attributed to acetone-iodoglycerol. Used for iodide therapy.

ALIZANTHRENE NAVY BLUE, Yellow R, *v.* ANTHRAQUINONE DYESTUFFS.

ALIZARIN AND ALLIED DYESTUFFS. *See also* articles on ANTHRACENE, CHAY ROOT, MADDER, METHYL ANTHRACENE, and VAT DYES.

	Sections
Development of Alizarin Dyestuffs Industry	1–3
Manufacture of Intermediates	4–8
Anthraquinone Sulphonic Acids	6
Aminoanthraquinones	8
Hydroxyanthraquinones	9–17
Alizarin	12–13
Mordant Dyestuffs derived from Alizarin	18–20
Acid Wool Dyes	21–22

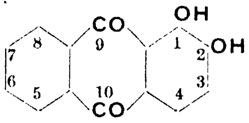
Alizarin is a colouring matter which was isolated by Colin and Robiquet in 1826 from the root of the madder plant *Rubia tinctorum*, a member of the order *Rubiaceæ*.

The art of dyeing with madder was known to the early Indians, Persians and Egyptians, and the madder plant was cultivated in Asia for some thousands of years. With the introduction of synthetic alizarin in the nineteenth century the natural product was soon displaced from the market and the cultivation of madder has now practically ceased.

Alizarin is not itself a dye, but it forms insoluble pigments or lakes with metallic hydroxides, which in the process of dyeing with alizarin are deposited on the fibres of the cloth. It gives the familiar "Turkey Red" on cloth that has been treated with aluminium hydroxide and Turkey Red oil.

In the pure crystalline state alizarin forms orange-red prisms or needles which melt at 289°C.

Alizarin is related chemically to the phenols and to the quinones. It has the formula $C_{14}H_8O_4$, and its chemical properties are indicated by the formula:



1 : *2-dihydroxyanthraquinone.*

1. DEVELOPMENT OF ALIZARIN DYESTUFFS INDUSTRY.

Synthesis of Alizarin.—Following the isolation of alizarin from madder in 1826, the way was prepared for the synthetic production of alizarin by the work of Schunck and of Strecker, who assigned to alizarin the formula $C_{14}H_{10}O_4$ and showed that it was related to naphthaquinone.

In 1868, when Graebe was beginning his research on quinones, his attention was turned to alizarin by some work of Martius and Griess on a hydroxy-naphthaquinone which they believed to be isomeric with alizarin. Graebe submitted alizarin to a distillation with zinc dust, and obtained from it the hydrocarbon *anthracene*, which had been isolated by Dumas and Laurent from coal tar. He therefore concluded that alizarin must be a hydroxyquinone of anthracene, the relation of these substances to one another being seen from the following formulæ:

$C_{14}H_{10}$	$C_{14}H_8O_2$	$C_{14}H_6O_2(OH)_2$
(Anthracene)	(Anthraquinone)	(Alizarin)

Having thus obtained anthracene from alizarin, Graebe proceeded to try to reverse the operation and convert anthracene into alizarin. The oxidation of anthracene to anthraquinone had already been effected by Anderson in 1862, and Graebe and Liebermann therefore attempted to introduce the hydroxyl groups by bromination followed by alkali fusion of the bromo-compound.

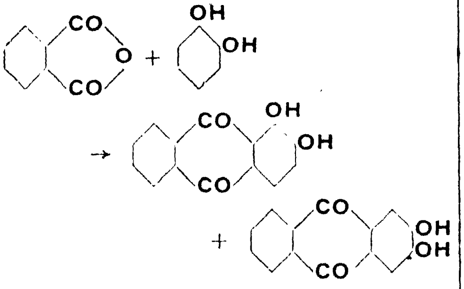
By heating anthraquinone with bromine in a sealed tube it was converted into 2 : 3-dibromo-anthraquinone:

$$C_{14}H_8O_2+2Br_2 \rightarrow C_{14}H_6O_2Br_2+2HBr.$$

On heating this substance with potassium hydroxide it gave the potassium salt of alizarin $C_{14}H_6O_2(OK)_2$ from which alizarin was obtained by decomposition with hydrochloric acid.

This synthesis of alizarin by Graebe and Liebermann in 1869 was recognised as one of the most outstanding successes of organic chemistry, since it was the first time that the artificial production of a vegetable colouring matter had been achieved. From a chemical point of view, the most remarkable fact in this synthesis is that Graebe and Liebermann's 2 : 3-dibromoanthraquinone on treatment with potash should yield alizarin, in which the hydroxyl groups occupy the 1 : 2-positions.

That the hydroxyl groups in alizarin are *ortho* to each other has been shown more recently by its synthesis, together with 2 : 3-dihydroxyanthraquinone, from phthalic anhydride and catechol.

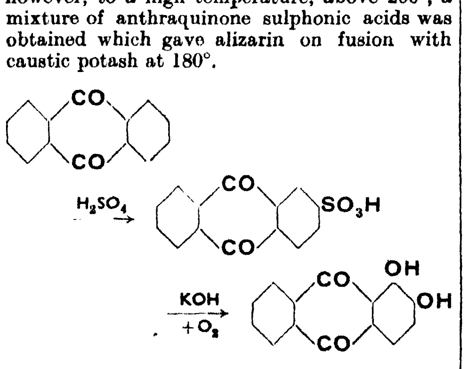


The fact that both alizarin and quinizarin (1 : 4-dihydroxy-anthraquinone) give the same substance, purpurin, or 1 : 2 : 4-trihydroxyanthraquinone, on oxidation with manganese dioxide shows that the hydroxyl groups in alizarin occupy the 1 : 2-positions.

The great importance of alizarin as a colouring matter led Graebe and Liebermann to patent their process of production, but owing to the cost of bromine, it proved to be too expensive to use for the manufacture of alizarin.

A cheaper method of production was perfected in the next year (1869) by W. H. Perkin (senr.) and simultaneously by Caro, Graebe and Liebermann, and by Rieser. In this process a sulphonic acid of anthraquinone was used instead of the bromo-derivative.

The great obstacle in carrying out this synthesis, in the first instance, was the remarkable stability of anthraquinone towards sulphuric acid, in which it dissolves in the moderately hot acid without change, and crystallises out again on cooling. By heating the solution however, to a high temperature, above 200°, a mixture of anthraquinone sulphonic acids was obtained which gave alizarin on fusion with caustic potash at 180°.



Perkin showed that the alizarin was formed from a *mono*sulphonic acid by oxidation during the alkali fusion, and not from a *di*sulphonic acid as might have been expected. The sulphonic acid gives on alkali fusion in the first place 2-hydroxyanthraquinone, which readily undergoes oxidation to alizarin. The two disulphonic acids which were also present in small amount in the mixture gave rise, also by oxidation, to flavopurpurin and anthrapurpurin, or 1 : 2 : 6- and 1 : 2 : 7-trihydroxyanthraquinones.

By the use of the anthraquinone sulphonic acid instead of the dibromo-derivative, a process had been perfected by which alizarin could be manufactured in quantity from the anthracene in coal tar, and at so low a price as entirely to supersede the old method of dyeing with madder.

Patents were applied for on June 25, 1869, by Caro, Graebe and Liebermann, and on the next day by W. H. Perkin.

Another process for the manufacture of alizarin discovered shortly afterwards by W. H. Perkin, and extensively used by him on a manufacturing scale, is the following :

Anthracene is treated with chlorine and thus converted into the well defined crystalline compound 9 : 10-dichloroanthracene.

This substance combines with Nordhausen sulphuric acid, forming a bright green solution containing a sulphonic acid of dichloroanthracene which on heating with sulphuric acid undergoes a remarkable change ; hydrogen chloride and sulphur dioxide are evolved, and sulphonic acid derivatives of anthraquinone are formed which, on fusing with caustic potash, yield a mixture of hydroxyanthraquinones containing alizarin.

Although other methods for the production of alizarin have since been devised, the main bulk of the alizarin of commerce is still obtained from "silver salt," the name given in the works to sodium anthraquinone-2-sulphonate.

An important technical improvement in the process was introduced by Koch, in 1873, who added such oxidising agents as sodium nitrate or chlorate to the alkali melt, instead of leaving the oxidation to the oxygen of the air.

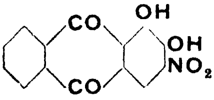
Later, by replacing the sulphuric acid by oleum containing anhydrous sulphur trioxide, it was found possible to obtain a greatly increased yield of the anthraquinone-2-sulphonic acid.

After Perkin's retirement from business in 1874 the world's trade in alizarin passed into German hands, and in 1881 the German makers of alizarin combined and advanced the price, clearing a sum of approximately £1,000,000 in one year on the manufacture of this dye.

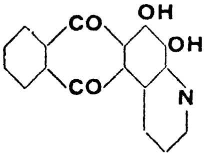
In 1882, just before the alizarin patent expired, the German combine issued a circular stating that they would cease to export alizarin unless the British consumers were willing to contract ahead for German alizarin at 2*s.* 6*d.* a pound ; the British Alizarin Company was then formed with the result that the price of alizarin fell to 4½*d.* a pound.

2. Colouring Matters Allied to Alizarin.

From these early beginnings the chemistry and the manufacture of the alizarin and the anthraquinone colours have developed step by step. The observation by Strobel that fabrics dyed with madder turned orange in nitrous fumes led to an investigation by Rosenstiehl, who showed that the orange colour was due to 3-nitroalizarin. This was introduced into commerce in 1876 under the name of *Alizarin Orange.*



Alizarin Orange.



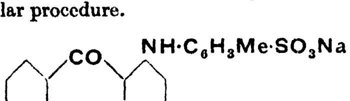
Alizarin Blue.

By heating 3-nitroalizarin with glycerol Prud'homme discovered *Alizarin Blue,* which was shown by Graebe and Liebermann to have the constitution of an anthraquinone-quinoline. (This investigation led to the discovery of the Skraup quinoline synthesis.)

In 1886, when the chemistry of the anthraquinone colours seemed to have reached its full development, Bohn discovered the method of direct hydroxylation by the use of fuming sulphuric acid, which gave a new impetus to investigation. The same reaction was discovered independently by R. E. Schmidt, and the Bohn-Schmidt reaction led to the discovery of a whole new series of valuable hydroxyanthraquinones and derived colours. By applying this reaction to Alizarin Blue, Bohn prepared *Alizarin Green* and *Alizarin Indigo Blue,* while Schmidt's investigations led to the production of the *Bordeaux, Alizarin Cyanin,* and *Anthracene Blue* colours.

Laubmann's discovery in 1893 of *acid wool dyes* of this series, containing a sulphonic acid group, which would dye wool directly and could be chromed afterwards, was a further important advance. The first of these to be marketed was the *Acid Alizarin Blue GR,* obtained from anthrachrysone (1 : 3 : 5 : 7-tetrahydroxyanthraquinone) by disulphonation, dinitration and reduction.

These investigations paved the way for the discovery in 1897 of *Alizarin Saphirol* and of *Alizarin Cyanine Green I,* which was obtained from quinizarin (1 : 4) by the exchange of *p*-toluidino-groups for the hydroxyl groups, followed by sulphonation of the product. A large number of acid wool dyes of great brilliance and fastness are obtained from quinizarin by a similar procedure.


CO
$NH{\cdot}C_6H_3Me{\cdot}SO_3Na$
CO
$NH{\cdot}C_6H_3Me{\cdot}SO_3Na$

An important advance in the technical production of these colouring matters was the introduction by Schmidt in 1895 of the use of *boric acid* for controlling the hydroxylation, nitration and sulphonation of anthraquinones, and in 1903 a further advance was the discovery that anthraquinone-1-sulphonic acid can be prepared by the sulphonation of anthraquinone in the presence of *mercury* as a catalyst.

The discovery of the first important anthraquinone *vat dyes* in the years 1901 to 1906 opened up a new field of investigation which has not yet been exhausted. Of the vat dyes, *Indanthrone, Flavanthrone, Pyranthrone, Violanthrone,* and the *Caledon Jade Green* colours are of unexampled permanence and fastness. The *acylaminoanthraquinone* vat dyes or *Algol* colours introduced by Schmidt have also attained considerable importance.

The discovery of the aminoanthraquinone *acetate silk dyes* in the years following 1922 has opened up a further important outlet for anthraquinone colours. The *Ionamine Blues,* derivatives of diaminoanthrarufin and of diaminochrysazin, introduced by Green and Saunders, have been followed by a series of aminoanthraquinone derivatives in the "*Duranol,*" "*Celatine,*" and "*S.R.A.*" series of acetate silk colours.

From the above account it may be seen that the anthraquinone dyes fall into four main classes :

(*a*) *Mordant Colouring Matters.* These, which include alizarin and many other hydroxyanthraquinones, require the use of a metallic hydroxide, or mordant, to fix the colours on the cloth.

(*b*) *Acid Dyes.*—The acid dyes, such as Alizarin Saphirol and Alizarin Cyanine Green, are usually the sodium salts of sulphonic acids, and dye wool or silk directly from a neutral or weakly acid bath.

(*c*) *Vat Dyes.*—These colours are insoluble in water, but are rendered soluble by reduction with sodium hyposulphite to their "leuco-compounds," which are used for dyeing (*see* VAT DYES).

(*d*) *Acetate Silk Dyes.*—These colours are insoluble in water, but may be "dispersed" in water by means of a sulphonated oil, such as sulphoricinoleic acid. They are taken up by acetate silk fibres from their colloidal suspensions.

A few dyes, such as Alizarin Red, may be used either as acid dyes or as mordant dyes, and a number of the acid dyes may be after-chromed, so that these two classes of dyes are not very sharply defined.

General Literature.—Thorpe and Linstead, "The Synthetic Dyestuffs and their Intermediate Products," London, 1933 ; J. Houben, "Anthracene und Anthrachinone," Leipzig, 1929 ; Fierz-David, "Künstliche organische Farbstoffe," Berlin, 1926 ; "Dyestuffs and Coal Tar Products," ed. by G. Martin, London, 1926 ; Thorpe and Ingold, "Vat Colours," London, 1923 ; "Anthracene and Anthraquinone," E. de B. Barnett, London, 1921 ; Horsfall and Lawrie, "The Dyeing of Textile Fibres," London, 1927 ; Harrison, "Lakes and Pigments," London, 1931.

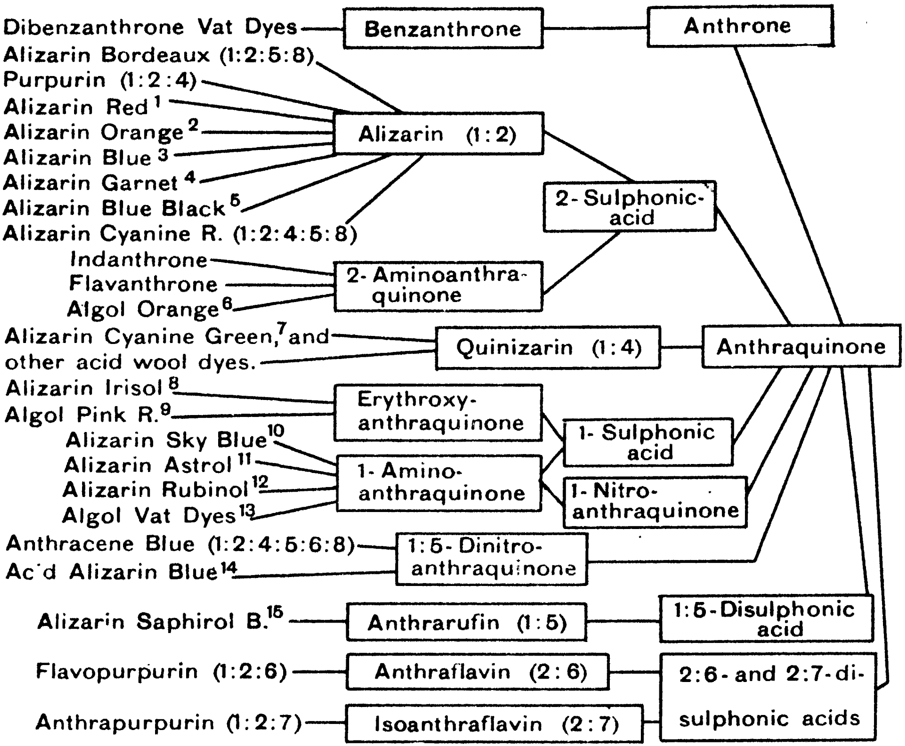


FIG. 1.

(1) Alizarin-3-sulphonic acid.
(2) 3-Nitro-alizarin.
(3) Alizarin-quinoline.
(4) 4-Amino-alizarin.
(5) Sulphonated condensation product of aniline and purpurin.
(6) 1, 2′-Dianthraquinonylamine.
(7) Sulphonated condensation product of *p*-toluidine and quinizarin.
(8) 1-Hydroxy-4-*o*-sulpho-*p*-tolylaminoanthraquinone.
(9) 1-Hydroxy-4-benzoylaminoanthraquinone.
(10) 1-Amino-2-bromo-4-*o*-sulpho-*p*-tolylaminoanthraquinone.
(11) 1-Methylamino-4-*o*-sulpho-*α*-tolylaminoanthraquinone.
(12) Anthrapyridone derivative.
(13) Acylaminoanthraquinones.
(14) 1 : 2 : 4 : 5 : 6 : 8-Hexahydroxyanthraquinone-3 : 7-disulphonic acid.
(15) 1 : 5-Dihydroxy-4 : 8-diaminoanthraquinone-2 : 6-disulphonic acid.

3. Nomenclature and Trade Names.

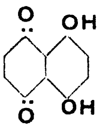
The name "alizarin" belongs, strictly speaking, only to 1 : 2-dihydroxyanthraquinone, but a number of related substances and mixtures of hydroxyanthraquinones, obtained for the most part by the alkali fusion of the anthraquinone sulphonic acids, are described in commerce by the name "alizarin." For example, while the Alizarin 3P. 20% (extreme blue shade) of the British Alizarin Company is a 20% paste consisting almost entirely of the 1 : 2-dihydroxyanthraquinone, the Alizarin YCA (BAC) 20% is a 20% paste consisting mainly of flavopurpurin (1 : 2 : 6-trihydroxyanthraquinone).

The term "alizarin" in composite names such as Alizarin Cyanine Green or Alizarin Black (which is a naphthaquinone derivative), is used to indicate some similarity to alizarin in dyeing properties, fastness or chemical constitution.

A complete list of the names and chemical constitutions of the alizarin colouring matters is to be found in the "Colour Index" (F. M. Rowe), 1924 and 1928, issued by the Society of Dyers and Colourists, or in "Farbstofftabellen," Schultz, 1928–34. A number of important alizarin colours and their relation to anthraquinone are shown in Fig. 1.

Amongst the best known colouring matters which bear the name "alizarin" but are not anthraquinone derivatives are the following :

Alizarin Black S (*BAC*) (*B*).—*Brilliant Alizarin Black* (*B*) is naphthazarin, which gives an intense black on a chromium mordant (Dimroth and Roos, Annalen, 1927, **456**, 180).



Alizarin Yellow (*MLB*).—Ellageic acid, occurs naturally and is a diphenyl derivative obtained by oxidising gallic acid.

Alizarin Yellow A (*B*) is 2 : 3 : 4-trihydroxybenzophenone.

Alizarin Blue RBN (*CCC*) is an isoxazine dye.

Alizarin Black SRA (*B*), *F* (*T*), *Acid Alizarin Black SE* (*MLB*), *and Alizarin Blue OCS* (*S*) are azo-dyes derived from β-naphthol.

4. MANUFACTURE OF INTERMEDIATES.

In England the main bulk of the alizarin colouring matters of commerce are manufactured from the anthracene of coal tar. The process generally used for the manufacture of alizarin itself is similar to the original method of Perkin, and of Graebe and Liebermann, in which the intermediates are anthraquinone and anthraquinone-2-sulphonic acid.

Purification of Anthracene.—See ANTHRACENE.

5. **Anthraquinone.**—Anthraquinone crystallises in pale yellow needles, m.p. 284·6°. It is insoluble in water and sparingly soluble in organic solvents. Anthraquinone may be readily obtained from anthracene by oxidation with chromic acid, ceric sulphate, ferric salts, halogens, nitric acid or nitric oxides. It may also be obtained by electrolytic oxidation.

Chromic acid is generally used technically as an oxidising agent. The oxidation of anthracene vapour by means of air in the presence of catalysts has also been effected and a process of this kind is reported to be in use by the I.G. Farbenindustrie. Various patents describe the oxidation of a 2% anthracene vapour-air mixture at 400°–430°, using contact masses containing boric acid and vanadium oxides (D.R.P. 397212, 408184 ; B.P. 335192).

The B.A.S. Fabrik succeeded in carrying out the technical oxidation of anthracene vapour with nitric oxides, but later reverted to the old chromic acid process owing to the value of the chromic sulphate which is produced as a by-product and which they were unable to produce so cheaply by any other method. The chromic sulphate is used largely for tanning leather. Should the chrome tanning process be superseded by the newer synthetic tanning materials it is probable that the chromic acid method of oxidising anthracene will disappear.

(*a*) *Chromic Acid Process.*—The oxidation of anthracene with chromic acid is carried out in large lead-lined vats fitted with lead-covered agitators and direct steam pipes also of lead. The capacity of the vats is usually 10,000-12,000 litres, but vats of 15,000–25,000 litres are not uncommon.

The anthracene must be in a finely divided condition, which is achieved by subliming it in a current of superheated steam and condensing with fine jets of water.

150 parts of sublimed anthracene are mixed with 3,000–4,000 parts of water, 300 parts of sodium bichromate are added and the mixture is heated to 75°. 900 parts of 50% sulphuric acid are then slowly run in in the course of 12 hours, the temperature at the same time being raised to the boiling-point.

Some frothing occurs owing to the formation of carbon dioxide by the oxidation of impurities, and if the anthracene used is very impure it may be necessary to work at greater dilution and add the acid more slowly.

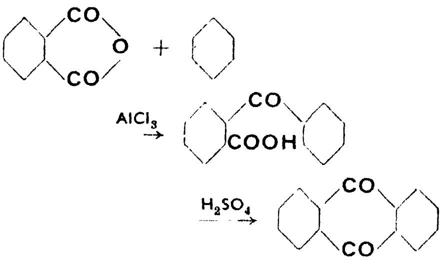
The oxidation requires 12–16 hours, during which the mixture may be agitated by means of a steam jet, using a Körting's injector. The progress of the reaction is tested by filtering a sample, washing and subliming it over a naked flame. With a little practice it is easy to distinguish the fine needles of anthraquinone from the silvery leaflets of anthracene. The absorption of chromic acid can also be ascertained by titration with ferrous sulphate.

When the operation is finished, the contents of the vat are run through a filter press, where the anthraquinone is thoroughly washed, the filtrate being collected in order to recover the chromium salt. 100 parts of good quality anthracene give a yield of 110 parts of anthraquinone.

Literature.—Davidson, "Intermediates for Dyestuffs," Benn, 1926 ; Grandmougin, Rev. prod. chim. 1917, **20**, 20 ; B.P. 413366.

(*b*) *Anthraquinone from Benzene and Phthalic Anhydride.*—In America and France anthraquinone is manufactured mainly by synthesis from benzene and phthalic anhydride, and this process is becoming of increasing importance in England for the manufacture of substituted anthraquinone derivatives.

Phthalic anhydride, which is obtained by the catalytic oxidation of naphthalene, reacts with benzene in the presence of aluminium chloride to give benzoyl-benzoic acid, and this on heating in concentrated sulphuric acid to 150° condenses to give anthraquinone.



The condensation with phthalic anhydride is carried out in practice in lead-lined vessels. It is started at 30° and the temperature is raised until no more hydrogen chloride is evolved. It is necessary to use two molecular proportions of aluminium chloride, as with a smaller proportion diphenyl-phthalide is formed through the interaction of a second molecule of benzene.

The yields in each stage of the reaction are almost quantitative, and the anthraquinone obtained is very pure. This process is likely to find still further application, since not only anthraquinone itself but a number of important anthraquinone derivatives are manufactured directly in this way. An example is the production on the large scale of 2 : 4-dichloro-1-aminoanthraquinone. Phthalic anhydride and *meta*-dichlorobenzene react to give 4′ : 6′-dichloro-*o*-benzoylbenzoic acid, which on nitration, reduction, and ring closure with sulphuric acid yields 2 : 4-dichloro-1-aminoanthraquinone.

The ring-closure is generally facilitated by reduction of the *o*-benzoyl-benzoic acid to the *o*-benzyl-compound, which is effected by means of zinc and ammonia. The I.G. Farbenindustrie describe the use of phosphorus pentoxide at 200° with copper oxide as a catalyst for the ring closure of *o*-3′-nitrobenzoyl-benzoic acid, which cannot be effected by sulphuric acid.

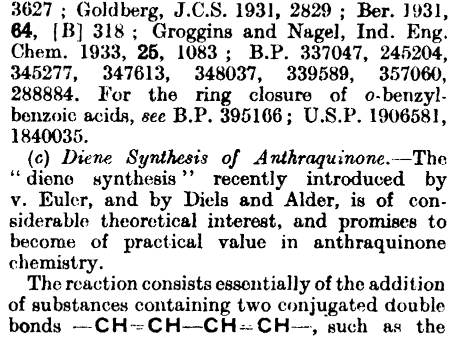
Literature.—Other recent syntheses by this method are given by Barnett and Low, Ber. 1931, **64** [B], 49 ; Gubelmann, Weiland and Stallmann, Ind. Eng. Chem. 1929, **21**, 1231. *See also* Heller and Schulke, Ber. 1908, **41**, 3627 ; Goldberg, J.C.S. 1931, 2829 ; Ber. 1931, **64**, [B] 318 ; Groggins and Nagel, Ind. Eng. Chem. 1933, **25**, 1083 ; B.P. 337047, 245204, 345277, 347613, 348037, 339589, 357060, 288884. For the ring closure of *o*-benzylbenzoic acids, *see* B.P. 395166; U.S.P. 1906581, 1840035.

(*c*) *Diene Synthesis of Anthraquinone.*—The "diene synthesis" recently introduced by v. Euler, and by Diels and Alder, is of considerable theoretical interest, and promises to become of practical value in anthraquinone chemistry.

The reaction consists essentially of the addition of substances containing two conjugated double bonds $-CH=CH-CH=CH-$, such as the butadienes, to substances such as maleic acid or quinones which contain the group

$$-CO-CH=CH-CO-.$$

For the synthesis of anthraquinone itself, α-naphthaquinone was heated with butadiene in alcoholic solution under pressure at 100° for 3–4 hours.



The resulting product, Δ^2-tetrahydroanthraquinone, was crystallised from ligroin and formed colourless crystals, m.p. 102°–103°. It gave anthraquinone on gentle oxidation with air or by means of chromic acid.

Using the less costly isoprene, 2-methylanthraquinone was obtained, and 2-chloroanthraquinone with 2-chlorobutadiene.

Literature.—Diels and Alder, Annalen, 1928, **460**, 98 ; B.P. 340509, 341553 ; D.R.P. 494433 ; Carothers, Williams, Collins, and Kirby, J. Amer. Chem. Soc. 1931, **53**, 4203.

Purification of Anthraquinone.—The crude anthraquinone obtained by the oxidation of anthracene must be carefully purified before it can be converted into the sulphonic acid. The processes commonly employed are as follows :

(*a*) *Sublimation.*—The anthraquinone is melted in iron pots and sublimed with a stream of superheated steam. The steam carries with it the vapour of the anthraquinone, which is obtained as a fine powder when condensed with a jet of cold water.

(*b*) *Use of solvents.*—Solvent naphtha and raw cresol are used technically as solvents for recrystallising anthraquinone, but many other solvents, *e.g.* acetone, pyridine bases and nitrobenzene have been suggested. A purification can also be effected by extraction with liquid sulphur dioxide or aniline or chlorbenzene.

(*c*) *Sulphuric acid process.*—The working of this method, which is largely used in this country, is based on the fact that crude anthraquinone dissolves in but is not acted on by sulphuric acid at 130°. The impurities, however, become converted into sulphonic acids which, being easily soluble, can be removed by treating the product with water, leaving nearly pure anthraquinone.

In carrying out this operation a mixture of 1 part of crude anthraquinone and 3 parts of sulphuric acid is placed in large circular lead-lined iron pots, and heated by steam for 24 hours, the whole being continuously agitated by a stirrer.

The dark coloured product is then run into shallow tanks, and exposed to the action of damp air or a gentle current of steam, until the acid has become diluted. In a short time anthraquinone separates out as a light-brown crystalline powder which, after washing with dilute soda and decantation, pressing and thoroughly drying, is found to contain about 95% of pure substance.

Other methods of purification depend on the reduction to the alkali-soluble anthrahydroquinone with zinc dust.

6. **Sulphonic Acids.**—*Sulphonation of Anthraquinone.*—The anthraquinone sulphonic acids are intermediates in the production of most of the alizarin colours and, consequently, the sulphonation of anthraquinone has been very thoroughly investigated. Anthraquinone is comparatively stable towards concentrated sulphuric acid and reacts only on heating to about 260°, when the 2- (or β-) sulphonic acid is formed. At higher temperatures a mixture of 2 : 6- and 2 : 7-disulphonic acids is formed. With 40% oleum sulphonation and disulphonation occur at lower temperatures, but otherwise the result is the same, and in the absence of a catalyst the main products are the 2-sulphonic acid and the disulphonic acids, only about 3% of the 1- (or α-) sulphonic acid being formed.

On the other hand, in the presence of 2% of *mercuric sulphate*, sulphonation gives rise almost entirely to the 1- or α-sulphonic acid which on further sulphonation yield the 1 : 5- and 1 : 8-disulphonic acids. Further sulphonation of the 2-sulphonic acid in the presence of mercury gives a mixture of the 1 : 6- and 1 : 7-disulphonic acids.

Fierz-David obtained by complete disulphonation in the presence of mercury 47% 1 : 5-, 27% 1 : 8-, 5% 1 : 6-, and 21% 1 : 7- disulphonic acids.

The action of mercury in the sulphonation of anthraquinone is probably due to its forming in the first place an α-mercuri-derivative. This group is then displaced by a sulphonic acid group to form the α-sulphonic acid.

If it be attempted to introduce more than two sulphonic acid groups into anthraquinone by the use of higher temperatures or stronger oleum, it is found that in general the sulphuric acid (or oleum) acts as an *oxidising* agent and forms sulphuric acid esters, which give hydroxyanthraquinones on hydrolysis (Bohn-Schmidt reaction). The sulphuric acid is simultaneously reduced to sulphur dioxide.

Properties of Sulphonic Acids.—The sulphonic acids are yellow in colour and easily soluble in water but less soluble in acids. In commerce they are generally found as their sodium salts. The sodium and calcium salts are for the most part not very soluble in water and show characteristic differences in solubility which are used in the separation of the acids. The insoluble arylamine salts are also very suitable for the separation and characterisation of the sulphonic acids.

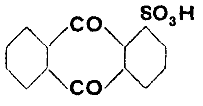
The importance of the sulphonic acids as intermediates in the production of the alizarin colouring matters is due to the mobility of the sulphonic acid groups in undergoing replacement by hydroxyl, amino and chloro-groups.

The sulphonic acids readily give hydroxyanthraquinones on heating with aqueous alkali. The reaction is nearly quantitative on heating with milk of lime under pressure. With caustic soda or potash the hydroxyanthraquinone first formed by replacement of the sulphonic acid group is generally oxidised further, as in the alizarin melt.

Aminoanthraquinones are obtained by heating the sulphonic acids with ammonia or amines. Replacement of the sulphonic acid group by chlorine is effected by boiling with aqueous hydrochloric acid and an alkali chlorate.

Literature.—Lauer, J. pr. Chem. 1931 [ii], **130**, 185 ; 1933 [ii], **137**, 161 ; 1933 [ii], **138**, 81 ; Schwenk and Waldman, Z. angew. Chem. 1932, **45**, 17 ; Fierz-David, Helv. Chim. Acta, 1927, **10**, 196 ; A. Meyer, Compt. rend. 1927, **184**, 609 ; Bull. Soc. chim. 1927, [iii], **41**, 1627.

Anthraquinone-1 (*or* α-) *Sulphonic Acid.*—The sulphonation of anthraquinone in the presence of mercuric salts to give the 1-sulphonic acid is carried out by heating 100 parts of anthraquinone for 3 hours at 130° with 110 parts of sulphuric acid containing 29% of sulphuric anhydride and 0·5 parts of mercury.

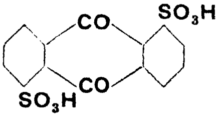


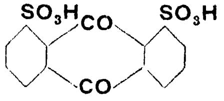
The sulphonation is conducted in large iron pots capable of holding 30 to 40 gallons. The conditions are such that part of the anthraquinone is left unsulphonated and is filtered off from the diluted solution at the end.

In the technical production of the sulphonic acids it is a common practice to use benzoylbenzoic acid as a starting material and effect the ring closure to anthraquinone and the sulphonation in one operation.

Anthraquinone-1-sulphonic acid is easily soluble in alcohol and water ; its lead, barium and strontium salts are sparingly soluble in hot water. The calcium salt crystallises from the hot solution. The potassium salt forms glistening yellow leaflets.

Anthraquinone-1 : 5- *and* 1 : 8-*Disulphonic Acids.*—The further sulphonation of the 1-acid in presence of mercury leads to the formation of anthraquinone-1 : 5-disulphonic acid, mixed with 1 : 8- and 1 : 7-acids. The same mixture is produced by the direct sulphonation of anthraquinone (100 parts) with 200 parts of sulphuric acid containing 40% sulphur trioxide, in the presence of mercury (1 part) at 160° for one hour. The mixture of acids is converted into the calcium salts and fractionally crystallised. The calcium salt of the 1 : 8-acid is least soluble; the middle fraction, which is the largest, consists of 1 : 5-, whilst the calcium salt of 1 : 7- is easily soluble.





Alternatively and preferably the acids may be separated by taking advantage of their different solubilities in sulphuric acid. For example, the reaction mixture obtained in the preparation described above would be mixed with 100–200 parts of sulphuric acid (60°Bé.), and the 1 : 5-acid thus obtained in crystalline condition is collected on asbestos. The 1 : 8-isomeride is precipitated from the filtrate on the addition of half its volume of water. Both acids are converted into potassium salts by adding potassium chloride to their hot aqueous solutions.

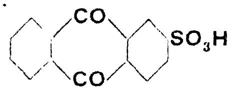
The success of these sulphonations depends very largely on the even distribution of the mercury catalyst throughout the mass and, to attain this end, the mercury may be introduced in the form of yellow mercuric oxide or a mercurous or mercuric salt, and intimately mixed with the anthraquinone employed in the operation. The discovery of a simple method of manufacture of these α-sulphonic acids of anthraquinone led to a great development in the anthracene series of dyes, especially in connection with the production of acid wool dyes of the type of Alizarin Saphirol and the Algol vat colours (*see* Vat Dyes).

The α-sulphonic acids may also be obtained by the oxidation of the sulpho-derivatives of anthracene. Thus anthracene α- and β-disulphonic acids yield anthraquinone-1 : 8- and 1 : 5-disulphonic acids respectively on treatment with nitric acid. Chlorine or bromine atoms in the alpha position in the anthraquinone nucleus may be displaced in favour of the sulpho-group by treatment of these halogen derivatives with aqueous sodium sulphite. Neither of these methods possesses technical importance.

Literature.—Liebermann and Dehnst, Ber. 1879, **12**, 1288 ; Iljinsky, Ber. 1903, **36**, 4194 ; Schmidt, Ber. 1904, **37**, 66 ; Fierz-David, Helv. Chim. Acta, 1927, **10**, 196 ; B.P. 10242, 13808; D.R.P. 157123, 164292 167169 ; Thorpe and Linstead, " The Synthetic

Dyestuffs and their Intermediate Products," 1933.

Anthraquinone-2- (or β-) Sulphonic Acid.—This acid is formed when anthraquinone is heated with fuming sulphuric acid *without* the addition of a catalyst :



It has not been found possible to conduct the sulphonation of anthraquinone in such a way that *only* the β-monosulphonic acid is produced. If the anthraquinone is completely sulphonated, considerable amounts of the disulphonic acids are simultaneously formed. In order to avoid this as far as possible the strength of the oleum used is adjusted so that the sulphonation stops when about 60 to 80% of the anthraquinone has been attacked.

The operation is conducted in large iron pots capable of holding from 30 to 40 gallons using 1 part of fuming sulphuric acid (containing 40 to 50 % SO_3) to 1¼ parts of anthraquinone. Oleum (20%) is first added to the anthraquinone and 38% oleum is added to the mixture until the concentration of anhydride is 26 to 27%. The mixture, which is stirred with iron stirrers, is heated by means of a steam-jacket to 135°–140° and kept at this temperature until about 60 to 80% of the anthraquinone has become sulphonated (7-9 hours). The mixture is poured into water, boiled and filtered from the unchanged anthraquinone. The product consists of 80% of the 2-sulphonic acid with about 20% of the 2 : 6- and 2 : 7-disulphonic acids in nearly equal proportions.

On partially neutralising the solution with soda the difficultly soluble sodium salt of anthraquinone-2-sulphonic acid separates in a mass of white, scaly crystals ("silver salt")· The sodium salt is filtered off and washed with brine. In this form it contains only 2–4% of the more soluble salts of the anthraquinone disulphonic acids.

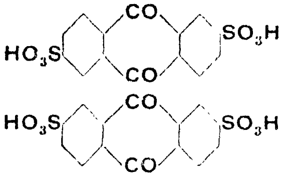
In the process described above it is often found difficult to filter off the unchanged anthraquinone from the sulphonic acid solution, as it separates in a slimy condition which is difficult to wash. This may be overcome by adding to the melt enough sulphuric acid to dissolve the unchanged anthraquinone. On slowly adding water the anthraquinone then separates in a crystalline condition in which it can easily be filtered (U.S.P. 1474507).

Silver salt crystallises with 1 H_2O ; 100 parts of water dissolve 5·59 parts at 18° and 18·88 parts at 100°. The free 2-sulphonic acid, obtained by acidifying a solution of the sodium salt, crystallises in plates. It is easily soluble in cold water and alcohol but insoluble in ether.

Large quantities of the 2-sulphonic acid are manufactured for conversion into 2-aminoanthraquinone, an intermediate in the Indanthrone and Flavanthrone vat dyes. It is of still greater importance as an intermediate in the production of alizarin, *q.v.*

Literature.—Davidson, "Intermediates for Dyestuffs," Benn, 1926 ; Schwenk, Z. angew. Chem. 1931, **44**, 912 ; Graebe and Liebermann, Annalen, 1871, **160**, 131 ; 1882, **212**, 44 ; Ber. 1874, **7**, 805 ; Dünschmann, Ber. 1904, **37**, 331 ; Crossley, J. Amer. Chem. Soc. 1915, **37**, 2178.

Anthraquinone-2 : 6- and 2 : 7-Disulphonic Acids.—In preparing the 2 : 6- and 2 : 7-disulphonic acids (or α- and β-disulphonic acids respectively) a mixture of anthraquinone and 20% oleum is heated to 160°, and 38% oleum is carefully added so that the temperature rises spontaneously to 175°–180°, at which it is kept until the end of the sulphonation. The weight of oleum employed is 200 to 220% of the weight of anthraquinone, and the final concentration of the oleum is 34 to 34½% SO_3. The solution is diluted and filtered into lead tanks and sodium sulphate added until the specific gravity reaches 32° to 33°Bé., when the sodium salt of the 2 : 6-disulphonic acid, which is less soluble, separates. It is filtered at 40° and washed with sodium sulphate solution.



The mother liquor containing excess sulphuric acid, sodium sulphate and the sodium salt of the 2 : 7-acid is treated with calcium carbonate in order to obtain the sodium salt of the anthraquinone-2 : 7-disulphonic acid.

The free acids obtained by decomposing the salts with acid are both readily soluble in alcohol and water but insoluble in ether and benzene ; the α-acid crystallises in small yellow crystals, the β-acid in beautiful yellow plates.

The salts of the α-acid are sparingly soluble in water and crystallise with difficulty ; those of the β-acid are readily soluble and crystallise with the greatest ease. The sodium salt of the α-acid crystallises with $7H_2O$, that of the β-acid with $4H_2O$.

7. **Nitroanthraquinones and other Intermediates.**—The nitration of anthraquinone leads in the first place to the formation of 1-nitroanthraquinone, and on further nitration to a mixture of 1 : 5- and 1 : 8-dinitroanthraquinones, in which the 1 : 5-isomer preponderates. The dinitration in sulphuric acid solution gives 40% of the 1 : 5-, 37% of the 1 : 8-, and 12–15% of the 1 : 6-dinitroanthraquinone.

1-Nitroanthraquinone and the 1 : 5- and 1 : 8-dinitroanthraquinones are manufactured on a large scale for the preparation of alizarin colouring matters. The 2-nitro-compound cannot be obtained by direct nitration.

Halogenoanthraquinones are readily obtained by the phthalic anhydride synthesis, in which both halogenated phthalic anhydride and the halogen derivatives of benzene may be used. The preparation of 2-chloroanthraquinone by this method is of technical importance. Imperial Chemical Industries, Ltd., obtain chloroanthraquinones by the chlorination of benzoyl-benzoic acid and ring closure without intermediate isolation of the chlorobenzoylbenzoic acids.

A very general method for the preparation of chloroanthraquinones is the treatment of the sulphonic acids with nascent chlorine. The sulphonic acid is boiled with aqueous hydrochloric acid and a solution of an alkali chlorate is slowly added. The sulpho-groups are replaced by chloro-groups, and the insoluble chloroanthraquinone separates from the solution. 1 : 5-Dichloroanthraquinone, which is used for the production of Indanthrene Violet RN, is obtained in this way from anthraquinone-1 : 5-disulphonic acid.

Literature.—Nitration of anthraquinone : Hefti, Helv. Chim. Acta, 1931, **14**, 1404. Preparation and orientation of dichloro- and trichloroanthraquinones : Goldberg, J.C.S. 1932, **73**, 83. Halogen-anthraquinones : Lauer, J. pr. Chem. 1933 [ii], **136**, 1 ; B.P. 389507. Sulphonation of 1-chloroanthraquinone : Thorpe and Goldberg, B.P. 373127 ; D.R.P. 495335.

Replacement Reactions.—In anthraquinone derivatives the substituents show a remarkable mobility, and many instances are known in which one group can be displaced by another. Almost all the 1-nitroanthraquinones are converted into the 1-sulphonic acids, for example, on heating with an aqueous solution of sodium sulphite (Schmidt, Ber. 1904, **37**, 66).

The 1-substituents are generally more mobile than the 2-substituents. Replacement reactions of this kind are used to a considerable extent in the production of the alizarin colouring matters.

If the sulphonic acids are heated with 80% sulphuric acid at 180° in the presence of mercury or boric acid, the sulphonic acid groups are eliminated and replaced by hydrogen. Here again the 1-sulphonic acid group is more mobile than the 2-derivative (Fierz-David, Helv. Chim. Acta, 1927, **10**, 225).

Sulphonic acid groups can also be eliminated by reduction with metals. α-Halogen atoms are fairly easily removed by reduction, but β-halogen atoms are much more firmly bound (Ullmann, Ber. 1912, **45**, 687).

The replacement of sulphonic acid groups by chlorine has already been described. Fierz-David has shown that in some instances this reaction can be reversed and 1-halogen atoms can be replaced by sulphonic acid groups by heating with sulphuric acid (D.R.P. 217552). The replacement of nitro-groups by chlorine is carried out by passing chlorine into a solution of the nitro-compound in sulphuric acid.

The replacement of the sulphonic acid group by fusion with caustic alkali is often accompanied by oxidation and the introduction of fresh hydroxyl groups, as in the alizarin melt. It has been found that α-sulphonic acid groups, nitro-groups, and halogen atoms can be replaced by hydroxyl without fear of oxidation by heating under pressure with milk of lime at 180°–190°. This reaction is of great value in the manufacture of the hydroxyanthraquinones. α-Halogen atoms may be replaced by hydroxyl simply by heating with concentrated sulphuric acid, and α-nitro-groups are replaced by hydroxyl on heating with aqueous pyridine.

Alkyloxy- and Phenoxy-anthraquinones can generally be prepared by heating the sulphonic acids or halogen or nitro-compounds, with potassium alkoxides or potassium phenate at about 200° ; the replacement of halogens in this way is catalysed by the addition of copper salts. α-Aryloxy-groups may be replaced by alkoxy-groups by treating with alcoholic potash at 80° (D.R.P. 538014). Thioether-groups may be introduced in a similar way by heating the sulphonic acids with alkali mercaptides.

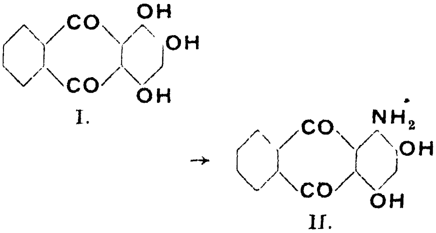
The replacement of the sulphonic acid group by the cyano-group by heating under pressure with potassium cyanide has been described (B.P. 359850).

The following table summarises the chief replacement reactions :

SO_3H NO_2 Cl	$Ca(OH)_2$	→	OH
	KOR	→	OR
	NH_3	→	NH_2
	RNH_2	→	NHR
SO_3H Cl	Cu	→	H
SO_3H	80% H_2SO_4	→	H
SO_3H	$HCl - HClO_3$	→	Cl
NO_2	Cl_2	→	Cl
α-OH	NH_3	→	NH_2
	RNH_2	→	NHR
α-NO_2	Na_2SO_3	→	SO_3H
α-Cl	H_2SO_4	→	SO_3H

8. Aminoanthraquinones (Acetate Silk Dyes).—The aminoanthraquinones are prepared (*a*) by the replacement of other substituents, as by heating the anthraquinone sulphonic acids, halogen derivatives, nitro-compounds or α-hydroxyanthraquinones with ammonia or amines ; (*b*) by the reduction of nitro-compounds, which is generally carried out by stirring with sodium sulphide in alkaline solution. Other methods, such as the reduction of diazo-compounds or the phthalic anhydride synthesis are of less importance.

The direct replacement of hydroxyl- by amino- or arylamino-groups is a reaction that is used to a great extent in the technical production of the acid wool dyes. It is found that in many cases an α-hydroxyl-group can be replaced by NH_2 simply by heating with aqueous ammonia. Purpurin (I), for example, forms 1-amino-2 : 4-dihydroxyanthraquinone (II) on heating under pressure with aqueous ammonia. In a similar manner quinizarin (1 : 4) forms 1 : 4-dianilinoanthraquinone on heating with aniline and boric acid. Leucoquinizarin condenses with aromatic amines still more readily (D.R.P. 144634 gives 22 examples of this reaction). When this process is applied to 1-hydroxyanthraquinone-2-sulphonic acids, the sulphonic acid groups are simultaneously eliminated.



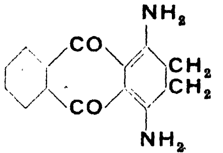
I.

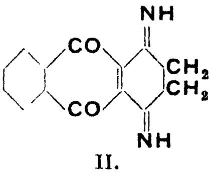
II.

It has been found that a number of the simpler aminoanthraquinones which are intermediates for the acid wool and vat dyes are themselves valuable dyes for cellulose acetate rayon (*see* Acetate Silk Dyes). A number of amino- and hydroxyamino-anthraquinone derivatives are included in the *Duranol*, *Celatine*, *S.R.A.*, and other series of dyes. These acetate silk dyes are devoid of affinity for cotton or pure cellulose fibres, but are readily taken up from their colloidal suspensions in water by cellulose acetate rayon, and give colours which are much faster to light than those which are obtained wtih azo dyes.

2-*Aminoanthraquinone*, which is an important intermediate in the manufacture of many anthraquinone dyes, is prepared by heating anthraquinone-2-sulphonic acid with 25% aqueous ammonia at 190°. The replacement of sulphonic acid groups by NH_2 has been investigated by Lauer (J. pr. Chem. 1932 [ii], **135**, 7). *See also* D.R.P. 480848 ; U.S.P. 1933236.

1 : 4-*Diaminoanthraquinone* is both an intermediate product in the preparation of the Alizarin Uranols as well as an acetate silk dye. It is formed as follows : 1 : 4-diamino-2 : 3-dihydroanthraquinone (I), obtained by heating leucoquinizarin with ammonia, is oxidised by manganese dioxide in sulphuric acid solution to give 1 : 4-diimino-2 : 3-dihydroanthraquinone (II), which on heating to 90°–100° gives 1 : 4-diaminoanthraquinone.


I.


II.

1-Aminoanthraquinone can also be converted into 1 : 4-diaminoanthraquinone by successive acylation, nitration, hydrolysis and reduction.

Literature.—Bamberger and Nawiasky, U.S.P. 1930351 ; B.P. 15355, 368829 ; Ber. 1906, **39**, 639.

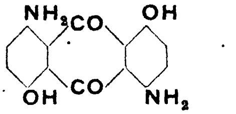
1 : 4 : 5 : 8-*Tetra-aminoanthraquinone*, which is a blue acetate silk dye, can be obtained from 1 : 4 : 5 : 8-tetrachloroanthraquinone, which is produced by chlorinating anthraquinone in ultra-violet light. It is also formed nearly quantitatively when Alizarin Saphirol B or SE is treated with ammonia and alkali hyposulphite under pressure at 70°–90°, or by treating 1 : 4 : 5 : 8-tetrahydroxyanthraquinone with ammonia. Alkylated aminoanthraquinones which are also dyes may be obtained similarly by using an alkylamine.

Literature.—I.C.I., B.P. 364141, 396976, 391859.

Alkylation plays an important part in modifying the shade in the aminoanthraquinone acetate silk dyes. By alkylating 1 : 4 : 5-triaminoanthraquinone and 1 : 4 : 5 : 8-tetra-aminoanthraquinone a number of different shades of blue are obtained. The violet 1-amino-4-methylaminoanthraquinone is prepared by the Soc. Chem. Ind. in Basle by heating 1-amino-4-methoxyanthraquinone with methylamine (B.P. 396662). The α-hydroxyethylamino-derivatives obtained by alkylating with ethylene chlorhydrin have also been described (B.P. 385202).

By varying the conditions of the condensation of leuco-hydroxyanthraquinones with ammonia, hydroxy-aminoanthraquinones may be obtained. For example, leuco-1 : 4 : 5 : 8-tetrahydroxyanthraquinone gives 1-hydroxy-4 : 5 : 8-triaminoanthraquinone on heating with ammonia and a little sodium hyposulphite at 120°. Similarly, dihydroquinizarinquinone gives 1-hydroxy-4-*p*-toluidino-anthraquinone on heating with *p* toluidine, and in the same way the other hydroxy-arylamino-anthraquinones which are used for the preparation of the Alizarin Irisols can be obtained (B.P. 396976, 380062).

4 : 8 *Diaminoanthrarufin*, which is the starting material in the manufacture of Algol Brilliant Violet 2R and 3R and Ionamine Pure Blue P, can be obtained from anthrarufin (1 : 5) by dinitration and reduction, but a much purer product is obtained by nitrating 1 : 5-diphenoxyanthraquinone (from anthraquinone-1 : 5-disulphonic acid and sodium phenate). Two nitro-groups first enter each phenoxy-group. The nitration then proceeds exclusively in the 4 and 8 positions of the anthraquinone nucleus. The resulting hexanitro-compound is readily hydrolysed by dilute alkali to give a very pure 4 : 8-dinitroanthrarufin, which yields the diaminoanthrarufin on reduction (D.R.P. 158531, 170728).



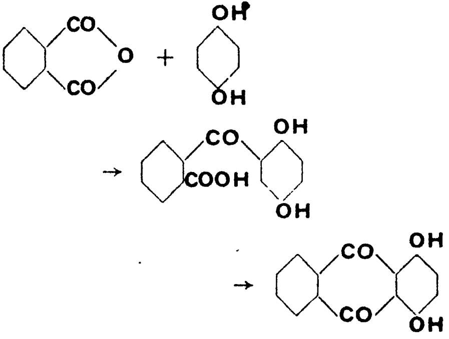
9. Hydroxyanthraquinones.

Position of OH-groups.	Name.	M.p. °C.
1	Erythroxyanthraquinone.	193
2	β-Hydroxyanthraquinone.	302
1 : 2	Alizarin.	289
1 : 3	Purpuroxanthin (Xanthopurpurin).	270
1 : 4	Quinizarin.	194
1 : 5	Anthrarufin.	280
1 : 7	*m*-Benzdioxyanthraquinone.	292
1 : 8	Chrysazin.	193
2 : 3	Hystazarin.	>360
2 : 6	Anthraflavin (Anthraflavic Acid).	>330
2 : 7	*iso*Anthraflavin (*iso*Anthraflavic Acid).	>330
1 : 2 : 3	Anthragallol (Anthracene Brown).	314
1 : 2 : 4	Purpurin.	257
1 : 2 : 5	Hydroxyanthrarufin (Alizarin Brilliant Bordeaux).	278
1 : 2 : 6	Flavopurpurin.	360
1 : 2 : 7	Anthrapurpurin (*iso*Purpurin).	369
1 : 2 : 8	Hydroxychrysazin.	239
1 : 2 : 3 : 5	α-Hydroxyanthragallol.	>350
1 : 2 : 3 : 7	β-Hydroxyanthragallol.	>380
1 : 2 : 4 : 6	Hydroxyflavopurpurin.	202

Position of OH-groups.	Name.	M.p. °C.
1 : 2 : 4 : 7	Hydroxyanthrapurpurin.	—
1 : 2 : 5 : 6	Rufiopin.	—
1 : 2 : 5 : 8	Quinalizarin (Alizarin Bordeaux).	>275
1 : 3 : 5 : 7	Anthrachrysone (Anthrachrysazin).	>360
1 : 2 : 4 : 5 : 8	Alizarin Cyanine R.	—
1 : 2 : 3 : 5 : 7	Dihydroxyanthragallol.	>360
1 : 2 : 3 : 5 : 6 : 7	Rufigallol (Rufigallic Acid).	282
1 : 2 : 4 : 5 : 6 : 8	Anthracene Blue.	—
1 : 2 : 4 : 5 : 7 : 8	Alizarin Hexacyanin.	—

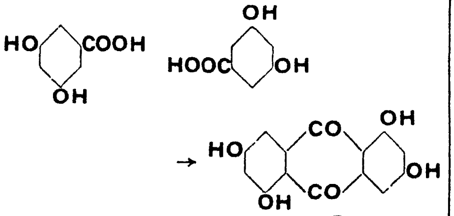
General Methods of Preparation.—Five main methods are used for the preparation of the hydroxyanthraquinones :

(*a*) *The Phthalic Anhydride Synthesis* can be applied to the preparation of hydroxyanthraquinones by condensing phthalic anhydride with phenols. Aluminium chloride or a mixture of sulphuric and boric acids is used as a condensing agent. The hydroxybenzoyl-benzoic acid can usually be isolated as an intermediate, and gives the hydroxyanthraquinone on heating with sulphuric acid.



This method has proved of great value in determining the constitutions of the hydroxyanthraquinones and in many cases excellent yields are given by this method, but difficulty is often experienced owing to phenolphthalein formation (Dimroth and Fick, Annalen, 1916, **411**, 321 ; Fairbourne and Gauntlett, J.C.S. 1923, **123**, 1137).

(*b*) *Synthesis from Hydroxy-benzoic Acids.*—Two molecules of a hydroxybenzoic acid are condensed together by heating in sulphuric acid solution. The method is of limited application, but a few substances such as anthrachrysone (I), rufigallol and anthragallol are manufactured in this way.



I.

(*c*) *Displacement Reactions.*—The replacement of halogens, sulphonic acid groups and nitro-groups by hydroxyl has already been described in Sec. 7 and is of considerable practical value. Erythroxyanthraquinone is manufactured from anthraquinone-1-sulphonic acid, for example, by heating under pressure with milk of lime.

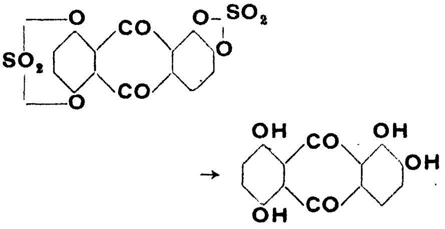
(*d*) *Oxidative Alkali Fusion of Anthraquinone Sulphonates.*—A typical example of this important reaction is the conversion of sodium anthraquinone-2-sulphonate (" silver salt ") into alizarin by fusing with caustic soda. In this case 2-hydroxyanthraquinone is first formed as an intermediate. Potassium chlorate or nitrate may be added as an oxidising agent.

The following are the chief technical applications of this reaction :

Anthraquinone-2-sulphonate→Alizarin (1 : 2)
Anthraquinone-2 : 6-disulphonate
→Flavopurpurin (1 : 2 : 6)
Anthraquinone-2 : 7-disulphonate
→Anthrapurpurin (1 : 2 : 7)
Anthraquinone-1 : 5-disulphonate
→Hydroxyanthrarufin (1 : 2 : 5)
Anthraquinone-1 : 8-disulphonate
→Hydroxychrysazin (1 : 2 : 8)

Xanthopurpurin gives purpurin and erythroxyanthraquinone gives a small yield of alizarin. The direct oxidation of anthraquinone to alizarin by this method has also been effected.

(*e*) *Oxidation of Anthraquinone or Hydroxyanthraquinones in Sulphuric Acid Solution ; Bohn-Schmidt Reaction.*—Anthraquinone reacts on heating with sulphuric acid to give in the first place the mono- and then the disulphonic acids. By treatment under more vigorous conditions with oleum in the presence of a catalyst such as selenium or mercury, it is found that the oleum acts as an oxidising agent, and sulphuric acid esters are formed which give hydroxyanthraquinones on hydrolysis :



The mono- and dihydroxyanthraquinones, such as alizarin, are oxidised by this method much more readily than anthraquinone itself. Some oleum is simultaneously reduced to SO_2.

The introduction of hydroxyl groups can be very largely directed by careful control of the temperature, the percentage of anhydride in the oleum, the catalysts added and the duration of the reaction. Boric acid is often added to moderate the reaction by forming boric acid esters with the hydroxyanthraquinones.

Closely comparable with oxidation with oleum is the oxidation in sulphuric acid solution by means of added oxidising agents such as manganese dioxide or nitrites (nitrosyl-sulphuric acid).

Manganese dioxide generally leads to the formation of an anthradiquinone, which can be reduced to the corresponding hydroxyanthraquinone with sulphur dioxide. With nitrosyl-sulphuric acid, which is prepared by slowly adding solid sodium nitrite to 15 parts of cold concentrated sulphuric acid, the oxidation is usually carried out at 180°–230° in the presence of boric acid. As in the oxidation with oleum, a catalyst such as mercuric oxide must be added, since no hydroxylation takes place with pure nitrosyl-sulphuric acid.

Hydroxylation with 80% oleum often leads to the formation of hydroxyanthraquinonesulphonic acids, but in general the sulphonic acid groups are readily eliminated by heating with 70% sulphuric acid, in the presence of mercuric oxide or boric acid.

The following oxidations by this method are typical :

Alizarin (1 : 2)—(SO_3 : HgO)
→Hydroxyanthrarufin (1 : 2 : 5)
Quinizarin (1 : 4) }
Alizarin (1 : 2) } —(SO_3 : HgO)
→Alizarin Bordeaux (1 : 2 : 5 : 8)
Erythroxyanthraquinone (1)—(SO_3 : HgO)
→Anthrarufin (1 : 5)
Anthraquinone—($NaNO_2$: HgO : B_2O_3)
→ { Quinizarin (1 : 4)
{ Anthrarufin (1 : 5)
Alizarin (1 : 2)—(MnO_2) →Purpurin (1 : 2 : 4)
Quinalizarin (1 : 2 : 5 : 8)—(MnO_2)
→Alizarin Cyanine R (1 : 2 : 4 : 5 : 8)

Oxidation with 80% oleum is used technically on a large scale for the production of the polyhydroxyanthraquinones containing 5 to 6 hydroxyl groups, such as Anthracene Blue. Noteworthy is also the production of Alizarin Green and Alizarin Indigo Blue from Alizarin Blue by oxidation with oleum.

Six hydroxyl groups can be introduced directly into anthraquinone, and in practice the main end-products from most of the hydroxyanthraquinones are the 1 : 2 : 4 : 5 : 6 : 8- and 1 : 2 : 4 : 5 : 7 : 8-hexahydroxyanthraquinones. The course of the reaction is determined in the works by spectroscopic examination. The fact that these oxidations cannot be made to go exclusively in any one direction explains the many different brands of mixed hydroxyanthraquinones on the market.

Literature.—D.R.P. 62018, 66153, 68113, 68114, 172688.

10. General Properties of the Hydroxyanthraquinones.

—The hydroxyanthraquinones are yellow, orange or red in colour. They may be characterised by their colours in solution in sulphuric acid, and by the colour change on adding boric acid which is due to the formation of boric acid esters.

Many of the hydroxyanthraquinones possess characteristic absorption spectra, and spectroscopic examination is a most valuable method of identifying them.

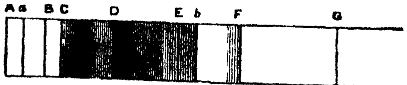


Fig. 2.—Absorption spectrum of alizarin in alcoholic potassium hydroxide solution.

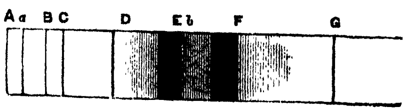
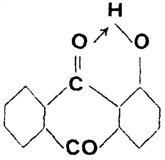


Fig. 3.—Absorption spectrum of purpurin in aluminium sulphate.

The usual procedure is to observe the absorption bands (*a*) in alcoholic solution, (*b*) in dilute potassium hydroxide, (*c*) in 95% sulphuric acid, and (*d*) in sulphuric acid with added boric acid. The wave-lengths of the absorption bands of a number of the hydroxyanthraquinones are given in Fierz-David, " Künstliche organische Farbstoffe," Berlin, 1926, and by Meek and Watson (J.C.S. 1916, **109**, 551) and Meyer and Fischer (Ber. 1913, **46**, 85).

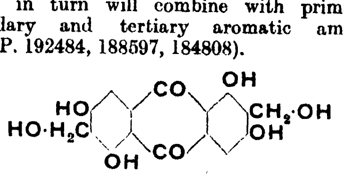
Most of the hydroxyanthraquinones can be sublimed. Alizarin sublimes at 110°, anthrapurpurin at 170°, flavopurpurin at 160°. By making use of this, alizarin may be quantitatively determined in a mixture of the three by heating to 140°, at which temperature only the alizarin sublimes.

Hydroxyl-groups in the 2- or β-position can readily be alkylated by reagents such as methyl iodide or dimethyl sulphate. Hydroxyl groups in the 1- or α-position are very difficult to alkylate, though alkylation can be effected by means of diazomethane (Perkin and Storey, J.C.S. 1929, 1399). This resistance of 1-hydroxyl-groups to alkylation is probably due to chelation with the carbonyl group, since 1-hydroxyl-groups can readily be alkylated when the carbonyl group is absent (Sidgwick and Callow, J.C.S. 1924, **125**, 527).



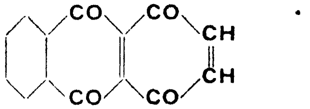
The hydroxyanthraquinones are easily benzoylated by means of benzoyl chloride, and in a number of instances by heating with 10–15 parts of benzoic acid. The acetyl derivatives, prepared by means of acetic anhydride, are useful for the purpose of identification.

The phenolic nature of the hydroxyanthraquinones is considerably modified by the presence of the kationoid carbonyl groups, but they still give a number of the typical reactions of phenols. Anthrachryson, for example, combines with formaldehyde to form the dicarbinol, which in turn will combine with primary, secondary and tertiary aromatic amines (D.R.P. 192484, 188597, 184808).



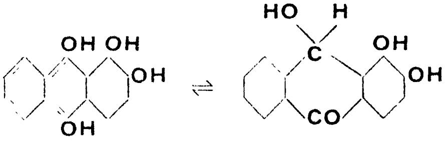
On treatment with sulphuric acid or weak oleum 1-hydroxyanthraquinone sulphonates in the 2-position, anthrarufin (1 : 5) gives anthrarufin-2 : 6-disulphonic acid, and alizarin gives alizarin-3-sulphonic acid. Treatment with strong oleum (80%) leads to oxidation, further hydroxyl groups being introduced.

Hydroxyanthraquinones containing two hydroxyl groups in the para-positions, *e.g.* **quinizarin** (1 : 4), are readily oxidised to the **anthradiquinones** by treatment with oxidising agents such as manganese dioxide, arsenic acid or lead peroxide in sulphuric acid solution. The 1 : 4 : 9 : 10-anthradiquinone which is obtained from quinizarin melts at 211°–213° and is readily reduced to quinizarin by sulphur dioxide (Dimroth and Schulze, Annalen, 1916, **411**, 345).

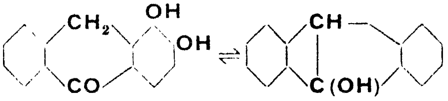


Owing to the readiness with which the hydroxyanthraquinones form lakes with metallic hydroxides, they are of value as qualitative tests for metals (Mikrochemie, Pregl Festschrift, **1929**, 77). A number of the hydroxyanthraquinones have been used as indicators. Alizarin gives a colour change in alcoholic solution from yellow to violet between p_H 5·5 and 6·8.

Reduction of Hydroxyanthraquinones.—Mild reduction with alkali hyposulphite gives in the first place the alkali salts of the leuco-derivatives, which are anthrahydroquinones, but can probably exist also as oxanthrones, the two forms being tautomeric.



The further reduction of the hydroxyanthraquinones to the anthrones or anthranols, which are also tautomeric, can generally be effected by heating with stannous chloride and aqueous hydrochloric acid.

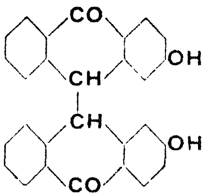


The yields are 60% or higher.

A. G. Perkin and his collaborators have made a thorough study of the reduction of the hydroxyanthraquinones, and have shown that in general the presence of an α-hydroxyl group exerts a retarding action on the reduction of the carbonyl to the anthranol, owing to chelation. The effect is diminished by a second β-hydroxyl group, as in alizarin, which is readily reduced to the anthranol (deoxyalizarin), in which the carbonyl group adjacent to the hydroxyl groups is reduced.

Hydroxyanthraquinones can be reduced to the anthrones by means of hydrogen and a nickel catalyst at 85°–90°/40 atm. Sodium hyposulphite in acetic acid solution has been used to reduce diacetyl-quinizarin to 1-acetoxy-4-hydroxy-10-anthrone.

The anthranols are of importance for the preparation of benzanthrones, which are used in the manufacture of the dibenzanthrone vat dyes. The hydroxyanthraquinones form dianthranyl derivatives on reduction with zinc and alkali with remarkable ease; for example, 2-hydroxyanthraquinone gives 2 : 2′-dihydroxydianthranyl.



A number of instances are known in which reduction under comparatively mild conditions causes the elimination of hydroxyl groups from the benzene nuclei. The reduction of purpurin, for example, with aluminium powder in sulphuric acid solution gives a good yield of leucoquinizarin. Reduction of purpurin with alkaline stannous chloride or sodium amalgam, on the other hand, gives purpuroxanthin.

Hydroxyl groups can sometimes be eliminated by treatment with nitrous acid. It has also been observed that 2-hydroxyanthraquinone is partially reduced to anthraquinone under the conditions of the alizarin melt if an oxidising agent is not added.

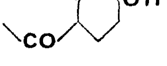
The hydroxyanthraquinones give anthracene on distillation with zinc dust.

Literature.—A. G. Perkin and collaborators, J.C.S. 1923, **123**, 2603 ; 1924, **125**, 470 ; 1925, **127**, 2684 ; 1930, 300 ; 1933, 1512 ; B.P. 353479, 349361 ; D.R.P. 296091.

Constitution of the hydroxyanthraquinones.—As there are seventy-five possible hydroxyanthraquinones it is understandable that not all of them have as yet been orientated. The method of greatest value in determining their constitutions is the synthesis by the phthalic anhydride method, in which, by the choice of suitable hydroxy-phthalic anhydrides and phenols a large number of hydroxyanthraquinones of known constitution may be synthesised. For example, the constitution of quinizarin is established by its synthesis from phthalic anhydride and hydroquinone. Hemipinic anhydride has also been used to synthesise a number of hydroxyanthraquinones containing hydroxyl groups in the 1- and 2-positions.

The fact that α-hydroxyl groups resist methylation by the usual reagents has been of great value in the determination of constitution, and frequent use has been made of the fact that hydroxyl groups adjacent to a carbonyl form crystalline compounds with boroacetic anhydride which can be isolated (Dimroth and Faust, Ber. 1921, **54** [B], 3020).

Colour and Lake Formation.—In spite of a great number of investigations, the problem of lake formation has not yet been fully solved. In general, those hydroxyanthraquinones which have two ortho-hydroxyl groups have mordant dyeing properties and form lakes, while those which have only one hydroxyl group adjacent to a carbonyl have feeble mordant dyeing properties. Attree and A. G. Perkin have shown that in general the group



is necessary for a good mordant dye (J.C.S. 1931, 146), *see* COORDINATION COMPOUNDS.

Liechti and Suida give the formula

$$Al_2O_3,CaO\cdot(C_{14}H_6O_2)_3H_2O$$

for the ordinary red aluminium-calcium lake of alizarin, but the Turkey Red oil which is added both in dyeing and in lake formation appears to perform more than a purely physical function (Dingl. polyt. J. **251**, 177). Many other formulæ for the lakes have been proposed.

Literature.—Morgan, J.C.S. 1922, **121**, 161 ; Dimroth, Annalen, 1926, **446**, 162 ; Sieber, Textilber. 1928, **9**, 579 ; Liepatoff, Textilber. 1928, **9**, 496 ; Victorow, J. Soc. Dyers and Col. 1928, **44**, 366 ; Williamson, J. Physical Chem. 1924, **28**, 891.

11. PROPERTIES OF INDIVIDUAL HYDROXYANTHRAQUINONES.

1-Hydroxyanthraquinone (Erythroxyanthraquinone) crystallises in orange needles, m.p. 193°. It is prepared technically by heating the sodium salt of anthraquinone-1-sulphonic acid under pressure with 10% milk of lime. Replacement of the sulphonic acid group by hydroxyl is almost quantitative on heating for 1 hour at 180°. It can also be prepared from 1-nitroanthraquinone by reduction, diazotisation and heating the diazo-compound.

It is formed, together with 2-hydroxyanthraquinone, when a mixture of phthalic anhydride and phenol is heated in sulphuric acid.

It has very weak mordant properties, and gives a red colour on chromed wool. It is of considerable value as an intermediate in the production of other anthraquinone derivatives.

On heating with acetic anhydride and sodium acetate it forms 1-acetoxyanthraquinone, m.p. 176°–179°, which crystallises from alcohol in yellow needles. 1-Methoxyanthraquinone, yellow needles, m.p. 140°–145°, is obtained by the action of boiling methyl alcoholic potash on 1-nitroanthraquinone.

Literature.—Baeyer and Caro, Ber. 1874, **7**, 969 ; Pechmann, Ber. 1879, **12**, 2128 ; Romer, Ber. 1882, **15**, 1793 ; Liebermann and Hagen, Ber. 1882, **15**, 1804 ; D.R.P. 197649, 172642, 97688.

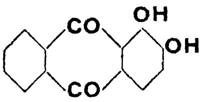
2-Hydroxyanthraquinone occurs naturally in Chay Root. It is prepared technically by heating anthraquinone-2-sulphonic acid with milk of lime. It crystallises from alcohol in yellow plates, m.p. 302°, and sublimes readily at a higher temperature.

It is formed, together with alizarin and purpurin, by the action of ammonium persulphate on a solution of anthraquinone in oleum.

A curious reaction of this hydroxyanthraquinone, involving the migration of an oxygen atom, is its conversion into quinizarin by treatment with nitrous acid in sulphuric acid solution in the presence of boric acid.

Literature.—Graebe and Liebermann, Annalen, 1871, **160**, 141 ; Baeyer and Caro, Ber. 1874, **7**, 969 ; Liebermann and Fischer, Ber. 1875, **8**, 975 ; Liebermann, Annalen, 1876, **183**, 208 ; Wacker, J. pr. Chem. 1896 [ii], **54**, 89 ; D.R.P. 86830.

12. Alizarin, 1 : 2-Dihydroxyanthraquinone.

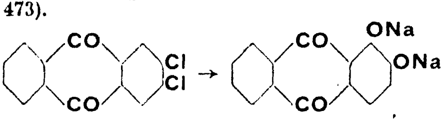


In the madder root alizarin occurs combined with sugar as a glycoside, *ruberythric acid.* Glycosides of alizarin are also found in Chay Root (*Oldenlandia umbellata*), and in certain species of *Galium* and rhubarb.

Alizarin may be obtained from ruberythric acid by fermentation with hydrolytic enzymes or by boiling with dilute acids. The sugar in ruberythric acid has recently been identified as 6-β-xylosidoglucose, or primverose, and ruberythric acid has been shown to be 2-*o*-β-primverosido-alizarin (Richter).

Alizarin has been prepared synthetically by a variety of methods. It is obtained, together with hystazarin (2 : 3), by heating catechol with phthalic anhydride in sulphuric acid solution at 200°. Under these conditions hystazarin undergoes isomeric change to alizarin in the course of a few hours.

Alizarin has also been synthesised from phthalic anhydride and *o*-dichlorobenzene. By treatment with aluminium chloride and ring-closure with sulphuric acid a good yield of 2 : 3-dichloroanthraquinone was obtained. This substance on fusion with alkali did not give hystazarin, as might have been expected, but formed alizarin (Philips, J. Amer. Chem. Soc. 1927, **49**, 473).



A similar synthesis from phthalic anhydride and *o*-chlorophenol, which formed 2-chloro-3-hydroxyanthraquinone, has been carried out by Tanaka.

Alizarin is formed in varying yields by the alkali fusion of both monohydroxyanthraquinones; 1-nitroanthraquinone, 2-aminoanthraquinone (together with indanthrene), 2 : 3-dibromoanthraquinone, and the mono- and *o*-disulphonic acids.

Anthraquinone may be oxidised to alizarin directly by treatment with ammonium persulphate in sulphuric acid solution, or by heating under pressure with aqueous potassium chlorate and potassium hydroxide.

Lagodzinski has obtained alizarin by oxidising 1 : 2-dihydroxyanthracene. It has been obtained by the condensation of hemipinic anhydride with benzene, by the reduction of rufigallol (1 : 2 : 3 : 5 : 6 : 7) with sodium amalgam, and it is formed in small amounts during the reduction of 1-nitroanthraquinone with sodium sulphide.

Manufacture of Alizarin.—(*a*) *Anthraquinone Process.*—The preparation and purification of the main intermediates in this process, anthracene, anthraquinone and anthraquinone-2-sulphonic acid, have been described in Sections 4–6.

In the conversion of "silver salt" (sodium anthraquinone-2-sulphonate) into alizarin by fusing with caustic soda, the sodium salt of 2-hydroxyanthraquinone is first formed. By the further prolonged heating with caustic soda this substance is converted into the disodium salt of alizarin. Sodium nitrate is added to provide the oxygen necessary for the oxidation involved in this reaction.

The fusion is conducted in large wrought-iron cylinders of 4,000 to 7,000 litres capacity, fitted with stirring gear and heated by hot air or superheated steam. The usual proportions of the ingredients in the charge are : 900 kg. silver salt, 190 kg. sodium nitrate, 1,260 kg. caustic soda, in 2,800 litres of water. The temperature is maintained at 180°–190° for a period of 50–70 hours, with a pressure of about 8 atmospheres inside the cylinder.

The product thus obtained is an intense purple fluid, which thickens on cooling and contains, besides the disodium salt of alizarin, sodium sulphite and an excess of caustic soda. The melt is run into water and acidified with sulphuric acid, when an orange precipitate of alizarin separates. The solution is boiled, allowed to settle, and the supernatant liquor run off. The alizarin is then washed in a filter press and made up into a 20% paste with water. The yield obtained is about 90%.

The sulphonation of anthraquinone is carried out in acid-resisting cast-iron vessels heated by superheated steam. The pots have a diameter of 1,165 mm., and height of 1,235 mm., and are surmounted by covers which are fitted with a manhole, stirrer, pipe for introducing pressure, thermometer tube, and a contrivance for the automatic registration of temperature. The anthraquinone used must be nearly chemically pure and should melt at 275°. Even small amounts of methylanthraquinone make it unsuitable for the manufacture of alizarin. 300 kg. of sublimed anthraquinone, 200 kg. of anthraquinone recovered from a previous sulphonation, and 400 kg. 20% oleum are heated for 8 hours at 145°. This procedure may be modified by introducing half the quantity of oleum and heating for 4 hours, after which the remainder is added in one or two portions in the course of three more hours. Before the reaction mixture cools it is forced into a lead-lined vat containing 1·5–2 cu. m. water, stirring continuously. The mixture is further diluted to 5 cu. m. and heated with direct steam. From 80 to 120 kg. of anthraquinone remain unattacked and are recovered by filtering through a press.

The filtrate is mixed with 85 kg. caustic soda, an amount which still leaves the liquor strongly acid, being only about $\frac{3}{8}$ of that theoretically required for neutralisation. The difficultly soluble silver salt separates and is collected in a press. The filtrate is submitted to vacuum evaporation to 22°–23°Bé. (measured while hot), and poured out into a vat provided with stirring apparatus, in which it crystallises. The process is aided if the vat is provided with a cooling-jacket. The silver salt is collected in a filter press and washed with brine, in which it is sparingly soluble. The yield of dry salt amounts altogether to 450–500 kg. It requires no further purification for the preparation of alizarin of bluish shade. The mother-liquor from the monosulphonate is neutralised with lime and the gypsum separated, after which the calcium salts are converted into sodium salts by means of sodium carbonate and the solution again filtered from chalk. Evaporation yields the 2 : 6-isomeride, and finally the 2 : 7-, but it is perhaps more general to blow the concentrated liquor directly into the alkali fusion apparatus. The fusion of silver salt with alkali is carried out in a series of horizontally placed cylinders provided with stirring gear and heated by means of superheated steam. They have to be capable of resisting a pressure of 12 atmospheres. The capacity is about 3,550 litres, and they are about 2,000 mm. long and have an inside diameter of 1,500 mm. The following example of a fusion may be regarded as typical : 1,687 cu. m. of caustic soda solution (45°Bé.) containing 1,030 kg. $NaOH$, together with 125 kg. saltpetre, are introduced into the pot and heated to about 125°, after which 625 kg. of moist silver salt (66·4%), corresponding to 415 kg. of the dry substance, are gradually added. The temperature is then raised to 180° and the pressure reaches 4–4·5 atmospheres. The product thus obtained is an intense purple fluid, becoming thick on cooling.

After 36–58 hours the process is usually complete. This is confirmed by testing a sample by boiling with milk of lime, filtering from the sparingly soluble calcium alizarate, and acidifying the filtrate, when an incomplete operation is indicated by the separation of golden flakes of β-oxyanthraquinone. The melt is diluted down to 6°Bé. in large lead-lined tanks, and acidified at 60° with sulphuric acid. For alizarin of especially blue shade the diluted alkali-fusion melt is treated in boiling solution with milk of lime until a drop of the liquid placed on filter-paper gives a clear red rim. The calcium salt is then separated and decomposed with hydrochloric acid. The precipitated alizarin is collected in filter presses and washed until the filtrate is free from acid. The press-cakes are analysed for content of anhydrous ash-free alizarin, and on the basis of the analysis a 20% paste is made in a special mixer made of pitch pine. The paste has a thin appearance, but if it should be desired thicker it suffices to add 0·5–1% of salt. The thickening of the paste which follows is a most singular phenomenon and resembles in appearance the salting out of a dye although, of course, the suspended solid is not increased in amount. For some Eastern markets a still thicker paste is prepared by the addition of glycerin, dextrin, molasses or starch. Alizarin in lumps of such a character that paste may be prepared from them as desired is made by mixing 20% paste with starch and then filtering off and very carefully and gradually drying the mixture. As much water as possible is removed by pressure and the remainder in a vacuum at a temperature not exceeding 60°. During the whole process of alizarin manufacture it is most important that the water used should be soft and as free as possible from iron. Iron in the water will completely ruin the value of a batch of alizarin from the point of view of purity of shade. If through some defect in the apparatus a batch should become contaminated it is useless to attempt to purify the dye by solution in alkali and reprecipitation with acid, in view of the circumstance that the objectionable iron derivatives (*cf.* the alizarin ferrates below) are reprecipitated along with the colouring matter. The best treatment is with hot dilute hydrochloric acid and just sufficient potassium chlorate to produce a clear yellow colour (*see*, Pohl, Ullmann, Enzyklopädie der technischen Chemie, 1928).

(*b*) *Dichloroanthracene Process.*—This process was introduced by W. H. Perkin and used by him for the manufacture of alizarin.

The anthracene used must be purified much more thoroughly than for the anthraquinone process. Leaden chambers are used for the chlorination of the anthracene. These are 10 ft. long, 4 ft. 6 in. wide, and 1 ft. 6 in. deep, and are used in pairs, connected at one end in order that any chlorine escaping from the first chamber may come in contact with a fresh amount of anthracene and thus prevent loss.

400 lbs. of anthracene are put into each chamber and subjected to the action of a rapid current of chlorine for about five or six hours.

The anthracene first fuses and gets dark in colour, hydrogen chloride being evolved in abundance, but after a time this fluid product begins to deposit crystals and soon becomes a semi-solid mass. In order to purify this crude product it is first freed from hydrochloric acid by washing with dilute caustic soda and then pressed between linen cloths in a hydraulic press. The yellow cakes of 9 : 10-dichloroanthracene thus obtained are soaked in coal-tar naphtha for some time and pressed, this operation being repeated until a product is obtained which contains 84% of pure substance.

The next process consists in converting the dichloroanthracene into the sulpho-acids of anthraquinone by treating it with ordinary concentrated sulphuric acid. This decomposition is accomplished in iron pots capable of holding about 30 gallons and fitted with iron covers in which there is an opening for the escape of the acid vapours formed during the reaction.

These pots are charged with 350 lb. of concentrated sulphuric acid and heated to 140°–160° by means of an ordinary fire, the dichloroanthracene (70 lb.) being introduced in small quantities at a time. After all the dichloroanthracene has been added and the frothing, due to the evolution of the hydrogen chloride and sulphur dioxide produced during the decomposition, has subsided the temperature is gradually raised to 260° and then maintained at this point until a sample taken out on a glass rod and diluted with water forms a nearly clear solution devoid of fluorescence.

The product contains now the mono- and disulphonic acids of anthraquinone, the latter of which greatly predominates. These crude sulphonic acids are next diluted with water in a large wooden tank and boiled with slaked lime until neutralised. The neutral product is then forced into filter presses to separate the calcium sulphate, the clear filtrate mixed with the washing of the calcium sulphate is evaporated until it contains about 15% of calcium salts, and then treated with sufficient sodium carbonate to precipitate all the calcium as carbonate. The solution of the sodium salts of the sulphonic acids is siphoned from the precipitated calcium carbonate, concentrated until it contains 30% of sodium salts and then converted into colouring matter by fusion with caustic soda, as described in the last process.

This process has now been abandoned in favour of the anthraquinone process, but a reinvestigation has recently been carried out by Minajew and Fedorow, who suggested a number of interesting improvements. The chlorination of anthracene was carried out in a mixture of technical *o*- and *p*-dichlorobenzene. 89 parts of anthracene were stirred with 206·5 parts of dichlorobenzene at 7°–9°C., while 36 parts of chlorine were passed in during a period of 6¼ hours. The excess of chlorine and hydrogen chloride were removed by a current of air, the solid allowed to settle, filtered and washed with alcohol. Yield 88% dichloroanthracene, m.p. 202°–203°. The dichloroanthracene was sulphonated by dropping 19·5% oleum into a suspension in nitrobenzene at 10°–12°. At the end of the reaction ice was added, the nitrobenzene removed in a current of steam and the sodium salt of the anthraquinone-2-sulphonic acid precipitated by the addition of alkali. This, on heating with caustic soda and potassium nitrate at 179°–183°, gave alizarin in 98% yield (Ber. 1930, **64** [B], 1143).

(*c*) *Direct Conversion of Anthraquinone into Alizarin.*—In the preparation of anthraquinone *β*-sulphonic acid it is very difficult to avoid the production of some disulphonic acid and, even if the alizarin is purified as described below, the shades obtained on mordanted fabrics are not quite identical with those given by the chemically pure dyestuff. The Badische Anilin und Soda Fabrik claim (D.R.P. 116526) that a remarkably pure alizarin, dyeing bluish shades of Alizarin Red on the usual alumina mordant, may be prepared from anthraquinone under the following conditions: Anthraquinone (100 parts) is heated with a solution of sodium or potassium hydroxide (300 parts) and sodium chlorate (20–30 parts) in water (100 parts) at 200° in an open vessel or autoclave until the oxidising agent is expended. The product is dissolved in water and air blown in in order to oxidise anthranols, and the alizarin is then precipitated by the addition of milk of lime. The precipitated salt is decomposed by hydrochloric acid, and the alizarin is separated from accompanying anthraquinone by dissolving in dilute aqueous sodium hydroxide and acidifying the filtered solution. Other processes have been suggested in which anthraquinone is heated with sodium or potassium hydroxide in the presence of sodium sulphite.

Literature.—Minajew and Fedorow, J. Chem. Ind. Russ. 1929, **6**, 535; D.R.P. 186526, 241806, 245987, 249369, 251236; Russ. Pat. 23391.

Iljinsky's Process.—An important technical improvement in the manufacture of the alizarin colouring matters, introduced by Iljinsky, has enabled the cost of their production to be considerably reduced. The sulphonation of the anthraquinone is carried out to completion, and the mixture of mono- and disulphonic acids is fused with caustic soda. The result is a mixture of alizarin, flavopurpurin and anthrapurpurin which are then separated through their calcium salts, so that all three are obtained comparatively pure (D.R.P. 140127, 140128, 140129, 194955, 137948).

Purification of Artificial Alizarin.—Commercial alizarin contains as impurities hydroxyanthraquinone, anthrapurpurin, flavopurpurin and small quantities of other colouring matters. In order to purify the alizarin the crude commercial product is dissolved in dilute caustic soda, and the solution treated with carbonic acid until two-thirds of the colouring matter has been precipitated as acid sodium salt. The precipitate is collected, washed with water, decomposed with hydrochloric acid, the crude alizarin thus obtained dissolved in caustic soda, and the treatment with carbonic acid repeated twice more. The purified product is then boiled with baryta water to remove hydroxyanthraquinone and anthraflavic acid (which dissolve), the barium salt of alizarin is collected, washed, decomposed by hydrochloric acid, and the alizarin either sublimed or recrystallised from alcohol.

Another method of separation is based on fractional sublimation (*see* Section 10). (*See also* Matsuoka, Bull. Chem. Soc. Japan, 1932, **7**, 50.)

13. Properties of Alizarin.

The importance of alizarin in dyeing is due to its extreme fastness to light. It is also absolutely fast to soap, acids and alkalis, so long as these do not attack the fibres on which it is deposited. On cloth mordanted with aluminium hydroxide and treated with Turkey Red oil, alizarin gives the familiar Turkey Red. With chromium it gives a dull purple, with iron a purple-black and with tin an orange-yellow.

Alizarin crystallises from alcohol in orange-red needles or prisms, which melt at 289°. With care it can be sublimed in magnificent deep red prisms, which may be obtained over an inch in length.

Alizarin dissolves in alkalis to give a deep purple solution from which it is completely precipitated by the addition of lime or baryta in the form of a blue precipitate of the calcium or barium salt.

Alizarin can readily be detected by means of the spectroscope as it gives two sharp absorption bands in alkaline solution. The following are the wave-lengths of the chief absorption bands given by alizarin :

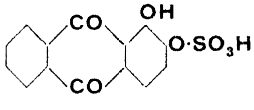
λ=610·8 *566·5* 527·6 in KOH.
624·9 *578·2* 537·1 in alcoholic KOH.
497·0 464·0 in H_2SO_4.
500·0 466·3 in H_2SO_4 and B_2O_3.

Alizarin is converted into purpurin (1 : 2 : 4) by heating with sulphuric acid at 225°. With oleum of moderate strength it gives alizarin-3-sulphonic acid. When fused with alkali hydroxides at a high temperature, benzoic acid and protocatechuic acid are formed. It is oxidised by concentrated nitric acid to phthalic and oxalic acids. On distillation with zinc dust it gives anthracene.

Alizarin is reduced to 2-hydroxyanthraquinone by stannous chloride and alkali. In Knecht and Hibbert's reduction method with titanous chloride for the estimation of reducible substances it is found that one molecule of alizarin requires four atoms of hydrogen for reduction.

On heating with acetic anhydride to 160° alizarin forms a diacetyl derivative, m.p. 184°; long yellow needles from alcohol.

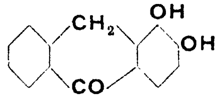
Alizarin forms the β-sulphuric acid ester on heating with a solution of sulphur trioxide in pyridine.



This ester has recently been found to be of value for dyeing alizarin colours on cotton. It is applied to the cotton mixed with aluminium sulphate and calcium acetate. On steaming there is a simultaneous liberation of alumina and alizarin on the fibre, and the dyeings obtained in this way are very fast to rubbing (B.P. 358465). The usual procedure in dyeing with alizarin is described by Horsfall and Lawrie, "The Dyeing of Textile Fibres," 1927. *See also* DYEING.

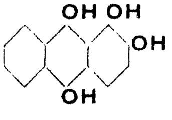
When heated under pressure with aqueous ammonia at 140°, alizarin forms 1-hydroxy-2-amino-anthraquinone-imide (Prud'homme, Bull. Soc. chim. 1906 [iii], **35**, 71 ; *ibid.* 666 ; Scholl and Parthey, Ber. 1906, **39**, 1201).

Deoxyalizarin, *Anthrarobin*, or 1 : 2-*Dihydroxyanthranol*, is formed when alizarin is



reduced with zinc and ammonia, or stannous chloride and hydrochloric acid. It crystallises from acetic acid and melts at 208°, and is easily reoxidised to alizarin. Owing to its reducing properties it is used medicinally in skin diseases. The anthranol and anthrone forms of the substance are tautomeric (A. G. Perkin and Goodall, J.C.S. 1924, **125**, 470; D.R.P. 117923).

Leucoalizarin 1 : 2-dihydroxy-anthra*hydro*quinone is obtained by reduction with sodium hyposulphite, and crystallises from acetic acid in brown plates which melt at 150° (Grandmougin, J. pr. Chem. 1907 [ii], **76**, 141).



Salts of Alizarin.—Calcium alizarate,

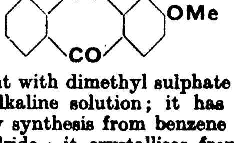
$$Ca(C_{14}H_6O_4)H_2O,$$

is precipitated as a purple mass on adding calcium chloride to an ammoniacal solution of alizarin. *Barium alizarate*, $Ba(C_{14}H_6O_4)H_2O$, is prepared, like the calcium salt, by mixing an alkaline solution of alizarin with barium chloride. It is deep violet when moist, almost black when dry, and very sparingly soluble in water. "*Aluminium alizarate*," which is obtained by precipitating an alkaline solution of alizarin with alum or aluminium hydroxide is a very fine red or rose-red precipitate. It is not a definite salt (Williamson, J. Physical Chem. 1924, **28**, 891). *Lead alizarate*, $(C_{14}H_6O_4)Pb$, is obtained by mixing an alcoholic solution of alizarin with an alcoholic solution of sugar of lead. *Alizarin ferric acid*, $Fe(C_{14}H_6O_4)_3H_3$, yields well crystallised sodium, ammonium and potassium salts. The latter crystallises with $8H_2O$, and is obtained by the addition of alcoholic potassium hydroxide to a mixture of alcoholic solutions of alizarin and ferric acetate.

Potassium hydrogen alizarate forms a compound with alizarin, brown-red crystals, $C_{14}H_7O_4K,C_{14}H_8O_4$, and a similar tripotassium dializarate has been described. These substances are analogous to the quadroxalates.

Literature.—Schunck, Annalen, 1848, **66**, 187 ; Anderson, Jahresber. Ges. vaterl. Kultur. 1847–8 (I), 749 ; Stenhouse, *ibid.* 1864, **17**, 543 ; Rochleder, Ber. 1870, **3**, 295 ; Perkin, J.C.S. 1870, **23**, 141 ; Graebe and Liebermann, Ber. 1870, **3**, 359 ; Baeyer and Caro, Ber. 1874, **7**, 972 ; Liebermann, Annalen, 1876, **182**, 206 ; Schunck, Annalen, 1848, **66**, 187 ; Wolff and Strecker, Annalen, 1850, **75**, 8 ; Lagodzinski, Ber. 1875, **28**, 1428 ; Widman, Ber. 1876, **9**, 859 ; Liebermann and Hohenemser, Ber. 1902, **35**, 1779 ; D.R.P. 116526 ; Perkin, J.C.S. 1899, **75**, 453 ; Knecht and Hibbert, J. Soc. Dyers and Col., Dec. 1915 ; Weinland and Binder, Ber. 1914, **47**, 977 ; Hofmann, Quoos, and Schneider, Ber. 1914, **47**, 1992 ; Heller, Z. angew. Chem. 1906, **19**, 669 ; Ber. 1908, **41**, 361 ; Tyrer, J.C.S. 1910, **97**, 1778 ; Hildebrand, Ellefson, and Beeve, J. Amer. Chem. Soc. 1917, **39**, 2301 ; Williamson, J. Physical Chem. 1924, **28**, 891 ; Phillips, J. Amer. Chem. Soc. 1927, **49**, 473 ; B.P. 174101, 246529 ; Tanaka, Chem. Zentr. 1927 (II), 2308 ; Liepatoff, Textilber. 1928, **9**, 496 ; Gebauer-Füllnegg and Eisner, Ind. Eng. Chem. 1928, **21**, 637 ; Minajeff and Fedorow, J. Chem. Ind. Russ. 1929, **6**, 535 ; Russ. Pat. 27750 ; Matsuoka, Bull. Chem. Soc. Japan, 1932, **7**, 50.

Derivatives of Alizarin.—*Alizarin β-methyl ether.* Alizarin readily gives the β-methyl ether



on treatment with dimethyl sulphate or methyl iodide in alkaline solution; it has also been prepared by synthesis from benzene and hemipinic anhydride ; it crystallises from alcohol, and melts at 224°–226°.

A. G. Perkin and Storey have attempted to prepare the α-methyl ether by treating 1-hydroxy-2-acetoxy anthraquinone with diazomethane. They obtained, however, not the expected 1-methoxy-2-acetoxy anthraquinone but 85% of the 1-acetylalizarin-2-methyl ether, an interesting migration of the acetyl group taking place (J.C.S. 1929, 1399).

The *dimethyl ether* can be obtained by reducing alizarin to deoxyalizarin and methylating the latter by means of methyl sulphate and sodium hydroxide in the usual manner. On oxidising the resulting product with sodium chromate and acetic acid alizarin dimethyl ether is obtained in golden yellow needles. It is identical with a product obtained from 2-hydroxyanthraquinone by successive methylation, nitration and treatment with methyl alcoholic sodium methoxide.

Alizarin diethyl ether can be prepared by heating alizarin with potash and potassium ethyl sulphate at 160° (Graebe and Thode, Annalen, 1906, **349**, 207 ; Perkin and Storey, J.C.S. 1928, 229).

3-*Bromoalizarin*, brown-red needles, m.p. 260°–261°, is obtained by the action of bromine on a solution of alizarin-3-sulphonic acid at 95°; it yields a pale yellow diacetyl derivative.

3-*Chloroalizarin*, m.p. 270°–271°, is prepared by the action of chlorine on a solution of alizarin-3 sulphonic acid. It gives a benzoyl derivative melting at 184° on benzoylation in pyridine.

3-*Iodoalizarin* has been obtained by the action of iodine on alizarin 1-methyl ether in boiling pyridine solution. It dyes yellower shades than alizarin (Perkin and Storey, J.C.S. 1931, 2620).

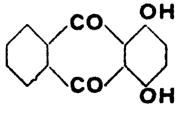
Purpuroxanthin (Xanthopurpurin), 1 : 3-Dihydroxyanthraquinone.—Purpuroxanthin exists in small quantities in madder. It may be synthesised by heating benzoic acid with 3 : 5-dihydroxybenzoic acid in sulphuric acid solution. It is easily obtained from purpurin (1 : 2 : 4) by reduction in alkaline solution.

Preparation.—Stannous chloride solution is added to a boiling solution of purpurin in 10% caustic soda until the solution loses its red colour and becomes yellow. Hydrochloric acid is then added, the precipitate filtered and washed with hydrochloric acid, and then dissolved in baryta solution. The filtered solution is reprecipitated with hydrochloric acid, and the purpuroxanthin crystallised from alcohol.

Purpuroxanthin crystallises in orange needles, m.p. 270°. It dissolves in alkalis to give a reddish solution which oxidises to purpurin on boiling in the air. It is not a mordant dyestuff.

Literature.—Schützenberger and Schiffert, Bull. Soc. chim. 1865, **4**, 12 ; Schunck and Römer, Ber. 1877, **10**, 172.

14. **Quinizarin, 1 : 4-Dihydroxyanthraquinone.**—Quinizarin is prepared technically by oxidising anthraquinone with a solution prepared by dissolving sodium nitrate, mercuric sulphate and boric acid in sulphuric acid, but



it is not easy to obtain a pure product by this method. A much purer quinizarin is obtained by chlorinating erythroxyanthraquinone in sulphuric acid solution and heating the 1-hydroxy-4-chloroanthraquinone so formed with boric and sulphuric acids, when the chloro-group is replaced by hydroxyl, giving quinizarin. Quinizarin may be prepared in the laboratory by heating a mixture of quinol or *p*-chlorophenol and phthalic anhydride in sulphuric acid solution. Equal parts of *p*-chlorophenol and phthalic anhydride are heated at 200°–210° for a few hours in 10 parts of sulphuric acid. The product is poured into three times its volume of water, and the precipitate filtered off, washed and pressed. The crude product is boiled with water to extract phthalic acid, dissolved in caustic soda, reprecipitated with hydrochloric acid and crystallised from alcohol. The small amount of purpurin which is nearly always present may be removed by washing with cold dilute caustic soda until the solution is no longer coloured red, and the residue is recrystallised from toluene.

Quinizarin is also formed when 1- or 2-hydroxyanthraquinone is heated in sulphuric acid solution with sodium nitrite and boric acid. It may be prepared from leucoquinizarin, which is obtained when purpurin (1 : 2 : 4) is reduced with aluminium powder in sulphuric acid solution. Dienel has obtained quinizarin from *a*-hydroxyanthracene through the 4-nitroso-derivative and 1 : 4-anthraquinone.

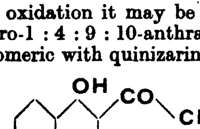
Quinizarin crystallises from alcohol in red needles, m.p. 194°, which sublime with partial decomposition at a higher temperature. It is easily soluble in benzene. The solutions in ether and in sulphuric acid show a fine greenish-yellow fluorescence. It dissolves in baryta to give a blue solution from which it is reprecipitated on passing in carbon dioxide (distinction from alizarin).

Quinizarin gives the following absorption bands : λ=*596·1*, 553·7, 517·7 in KOH ; 516·0, 502·1, *484·4*, 468·8, 453·9 in alcohol ; *548·3*, 509·6, 476·4 in H_2SO_4.

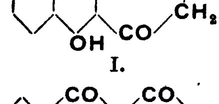
Quinizarin gives colours on fabrics mordanted with iron, chromium or aluminium which are about $\frac{1}{10}$ as deep as those produced by an equal weight of alizarin. It is not used as a dyestuff, but is a valuable intermediate in the production of the acid wool dyes.

When fused with potash, quinizarin forms hydroxychrysazin (1 : 2 : 8). Diacetyl-quinizarin melts at 200°.

Leucoquinizarin is obtained by reducing quinizarin with alkaline sodium hyposulphite, or by reducing purpurin with aluminium powder in sulphuric acid solution. It is a yellow crystalline substance melting at 135°. Zahn and Ochwat have shown that it has the constitution I. By careful oxidation it may be converted into 2 : 3-dihydro-1 : 4 : 9 : 10-anthradiquinone (II), which is isomeric with quinizarin.



I.



II.

It condenses with aromatic amines more readily than quinizarin itself, and for this reason is used in the manufacture of the acid wool dyes of this class.

Literature.—Baeyer and Caro (Ber. 1875, **8**, 152) ; Schunck and Römer (Ber. 1877, **10**, 554) ; Zahn and Ochwat (Annalen, 1928, **462**, 72) ; Dienel (Ber. 1906, **39**, 926) ; B.P. 209694, 245584, 256068 ; D.R.P. 81960, 81245, 81234, 161954, 162792.

2-*Nitroquinizarin* is obtained by nitrating quinizarin in acetic acid or nitrobenzene solution. It forms brick-red crystals, gives a cerise colour in sulphuric acid and dyes wool brown on an alumina mordant or violet-brown on chromed wool.

Quinizarin-2-sulphonic acid is obtained by the action of sodium sulphite on a hot aqueous suspension of quinizarin, preferably in the presence of an oxidising agent such as pyrolusite (Marshall, J.C.S. 1931, 3206).

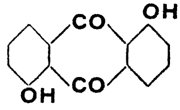
Fuming sulphuric acid (70–80% SO_3) converts quinizarin at 20°–40° into Alizarin Bordeaux (1 : 2 : 5 : 8) (Schmidt, Bull. Soc. chim. 1914 [iv], **15**, 1).

Dibromoquinizarin.—The hydrogen atoms in quinizarin are not easily substituted by halogens. An additive product, a hexabromide, is formed with bromine at 0°C. At 40° the product is bromoquinizarin-dibromide, and even at temperatures up to 230° only a dibromo-derivative is formed.

Dichloroquinizarines.—A number of the dichloroquinizarines have been prepared by condensing hydroquinone with dichlorophthalic anhydrides. 5 : 8-Dichloroquinizarin crystallises in brown-red needles, m.p. 266°. It reacts on heating with aniline to give 5 : 8-dianilino-quinizarin, m.p. 245°.

5 : 6-Dichloroquinizarin melts at 208°, and its diacetyl derivative at 140°. 6 : 7-Dichloroquinizarin melts at 288°, and its diacetyl derivative at 125° (Frey, Ber. 1912, **45**, 1358).

Anthrarufin, 1 : 5-Dihydroxyanthraquinone.—Anthrarufin is prepared technically by heating anthraquinone-1 : 5-disulphonic acid with milk of lime.



It is also obtained from anthraquinone by the Bohn-Schmidt reaction. 50 parts of anthraquinone are heated with 20 parts of boric acid and 1,000 parts of oleum (80% SO_3) for 36 hours at 100°.

Anthrarufin is formed, together with anthraflavin (2 : 6) and *m*-benzdioxyanthraquinone (1 : 7), when *m*-hydroxybenzoic acid is heated with sulphuric acid.

Anthrarufin crystallises in yellow needles, m.p. 280°. Absorption bands : λ=*570·7*, 557·7, *578·5*, 517·7, 487·1 in H_2SO_4. Anthrarufin sublimes easily above 280° (distinction from anthraflavin). It dissolves with difficulty in ammonia and soda but more easily in potash.

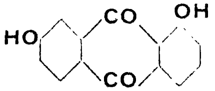
Anthrarufin is manufactured chiefly as a starting material for preparing Alizarin Saphirol

B. Diacetyl-anthrarufin melts at 244°–245°. Anthrarufin dimethyl ether is obtained by boiling 1 : 5-dinitroanthraquinone with methyl alcoholic caustic soda, m.p. 230°.

Literature.—Schunck and Römer, Ber. 1878, **11**, 1175 ;. Liebermann and Dehnst, Ber. 1879, **12**, 1289 ; Pleus, Ber. 1902, **35**, 2923 ; D.R.P. 101220.

1 : 6-Dihydroxyanthraquinone was the last of the dihydroxyanthraquinones to be obtained. It was prepared in 1907 by Frobenius and Hepp from 1-nitroanthraquinone-6-sulphonic acid, which was converted by sodium methoxide into 1-methoxyanthraquinone-6-sulphonic acid, and the latter hydrolysed to a hydroxyanthraquinone sulphonic acid by heating with sulphuric acid. The sodium salt was then prepared and heated with milk of lime at 195° under pressure. The substance crystallises in orange-yellow needles melting at 271°–272°, and dissolves in ammonia or potassium hydroxide to a yellow solution. Oxidation by heating under pressure with a solution of sodium hydroxide and sodium nitrate results in the production of flavopurpurin (1 : 2 : 6).

m-Benzdioxyanthraquinone (1 : 7-dihydroxyanthraquinone) is formed together with anthraflavic acid and anthrarufin by heating *m*-hydroxybenzoic acid with sulphuric acid. It is separated from these by treatment with benzene and subsequent recrystallisation from dilute alcohol. It forms yellowish needles which melt at 292° and sublime at a higher temperature with little decomposition.



It dissolves in alkalis with a dark yellow colour, and in sulphuric acid to give a brownish-yellow solution which shows no absorption bands.

Literature.—Schunck and Römer, Ber. 1878, **11**, 1176 ; Liebermann and Dehnst, Ber. 1879, **12**, 1289.

Chrysazin, 1 : 8-Dihydroxyanthraquinone is prepared technically by heating anthraquinone-1 : 8-disulphonic acid with milk of lime. It is also prepared from 1 : 8-dinitroanthraquinone.

Chrysazin forms reddish-brown needles, m.p. 193°. Absorption bands : λ=533·0, *495·6*, 465·9 in H_2SO_4. It dissolves with a red colour in alkalis and in sulphuric acid, and forms a diacetyl derivative, m.p. 227°–232°. It is sold as a purgative under the name *Istizin*.

The monopotassium salt of chrysazin separates on cooling the hot aqueous solution, in orange-red needles which contain water of crystallisation and form the violet anhydrous compound on heating to 100°.

On reduction with hydriodic acid and phosphorus, chrysazin forms the anthranol, m.p. 177°. The chlorination of a suspension of chrysazin in dilute sulphuric acid gives the 4 : 5-dichlorochrysazin. Chrysazinamide, 1-hydroxy-8-aminoanthraquinone, is obtained by saturating a chrysazin paste with ammonia at 0° and heating in a sealed tube.

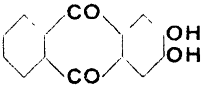
On sulphonating chrysazin with 20% oleum it forms a disulphonic acid. The nitration of chrysazin dimethyl ether (obtained by the action of sodium methoxide on 1 : 8-dinitroanthraquinone) gives a dinitro-chrysazin dimethyl ether.

The processes which are applied to anthrarufin (1 : 5) to convert it into Alizarin Saphirol B give a similar dye when applied to chrysazin.

Chrysazin also condenses with aromatic amines to give products which form acid wool dyes on sulphonation. In this respect there is a general similarity between chrysazin, quinizarin and anthrarufin.

Literature.—Schrubsdorff, Ber. 1902, **36**, 2936 ; Wobling, Ber. 1902, **36**, 2941 ; Nölting, J.S.C.I. 1898, 372 ; 1900, 342 ; 1906, 314 ; Chem.-Ztg. 1910, 977.

Hystazarin, 2 : 3-Dihydroxyanthraquinone.—Hystazarin occurs as the monomethyl ether in Chay Root. It may be prepared from phthalic anhydride and catechol.



Preparation.—5 grms. catechol, 6·8 grms. phthalic anhydride, and 75 grms. sulphuric acid are heated for 4½–5 hours at 140°–150°. (Alternatively, the mixture may be heated with 50 grms. sulphuric acid for ½ hour at 180°–200°.) The resulting product is poured while still warm into 750 ml. water, boiled and filtered hot. The precipitate is washed with hot water, dissolved in dilute potash, and the dark blue solution precipitated with acid. The precipitate is washed, dried, and treated with boiling alcohol in an extraction apparatus, whereby a considerable proportion is dissolved. The orange-red solution yields on evaporation a mixture of hystazarin and alizarin, which are separated by extracting with benzene, which dissolves the alizarin and leaves the hystazarin. The latter may be further purified by crystallisation from acetone. Yield : 1½% alizarin and 12% hystazarin of catechol used.

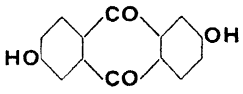
Hystazarin crystallises from acetone in orange-yellow needles, m.p. above 360°. The solution in alkalis is cornflower blue. Absorption bands : λ=619·8, 587·4 in KOH. The solution in sulphuric acid is red. On heating with sulphuric acid at 200° hystazarin is slowly converted into alizarin. Nitration with one molecular proportion of nitric acid in sulphuric acid solution gives 1-nitrohystazarin, which is converted into 1 : 4-dinitrohystazarin on further nitration.

Hystazarin possesses only very feeble tinctorial properties but produces a faint red colour on an aluminium mordant.

Reduction with zinc dust and ammonia gives 2 : 3-dihydroxyanthranol, m.p. 282°. Diacetylhystazarin melts at 205°–207°.

Literature.—Liebermann and Schoeller, Ber. 1888, **21**, 2501 ; Lagodzinski and Loretan, Ber. 1895, **28**, 118 ; Liebermann and Hohenemser, Ber. 1902, **35**, 1778 ; Schrubsdorf, Ber. 1903, **36**, 2936.

Anthraflavin, 2:6-Dihydroxyanthraquinone.—Anthraflavin is manufactured from anthraquinone-2 : 6-disulphonic acid by fusion with potash or by heating with milk of lime. It is generally present in artificial alizarin. It has also been obtained synthetically by heating *m*-hydroxybenzoic acid with sulphuric acid at 190°.



Anthraflavin crystallises from alcohol in yellow needles which melt above 330°. It sublimes with partial decomposition. It has no mordant dyeing properties. It dissolves in alkalis to give an orange solution, and gives a green solution in sulphuric acid, the absorption spectrum of which shows a broad band between the green and the blue. The sodium salt is sparingly soluble in water and crystallises much more readily than the sodium salt of *iso*anthrarufin, from which it can thereby be separated.

Anthraflavin is an intermediate in the manufacture of Erweco Alizarin Acid Blue and other acid wool dyes.

On treatment with nitric acid it forms a dinitro-derivative, and a tetranitro-derivative which explodes without melting on heating to 307°. With acetic anhydride it forms a diacetate, m.p. 228°–229°.

Literature.—Perkin, J.C.S. 1871, **24**, 1109 ; 1872, **26**, 19 ; Schunck and Römer, Ber. 1876, **9**, 379 ; 1878, **11**, 970 ; Liebermann, Ber. 1872, **5**, 968 ; Rosenstiehl, Bull. Soc. chim. 1903, [iii], **29**, 401–434.

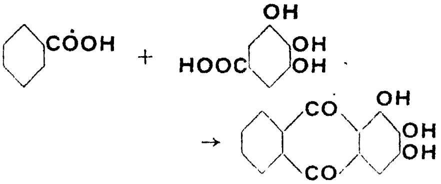
***iso*Anthraflavin, 2:7-Dihydroxyanthraquinone.**—*iso*Anthraflavin is formed when anthraquinone-2 : 7-disulphonic acid is fused with potash. It is generally contained in crude artificial alizarin, from which it may be isolated. The crude alizarin is dissolved in dilute caustic soda, the solution precipitated with hydrochloric acid, and the precipitate dissolved in cold baryta water and filtered. (In this way *iso*anthraflavin, which forms a soluble barium salt, is separated from alizarin, anthrapurpurin and anthraflavin, which give insoluble barium salts). The filtrate is treated with hydrochloric acid, and the precipitate crystallised from alcohol.

*iso*Anthraflavin crystallises in long yellow needles containing $1H_2O$, which can be driven off at 150°. It melts above 360° and sublimes at a high temperature in lustrous yellow needles, and forms a diacetate, m.p. 195°. It dissolves easily in alkalis forming a deep red solution ; it does not dye mordanted cloth. Fused with potash, *iso*anthraflavin yields anthrapurpurin (1 : 2 : 7).

Literature.—Schunck and Römer, *Ber.* 1876, **9**, 379.

15. TRIHYDROXYANTHRAQUINONES.

Anthragallol, Anthracene Brown FF, 1:2:3-Trihydroxyanthraquinone.—Anthragallol is manufactured together with rufigallol by heating a mixture of gallic acid (1 part), benzoic acid (2 parts), and sulphuric acid (20 parts) to 125° for eight hours. The product is poured into water, well washed, and recrystallised from alcohol.



Anthragallol does not itself occur in nature, but its three isomeric dimethyl ethers have been found in Chay Root.

It may be obtained from 1 : 3-dinitro-2-hydroxyanthraquinone (the nitration product of 2-hydroxyanthraquinone) by reduction in strongly alkaline solution. Or 1 : 3-diamino-2-hydroxyanthraquinone may be converted to anthragallol by heating with hydrochloric acid under pressure.

Anthragallol crystallises in yellow needles which sublime without melting at 290°. It is sparingly soluble in water, chloroform or carbon disulphide ; readily soluble in alcohol, ether or glacial acetic acid.

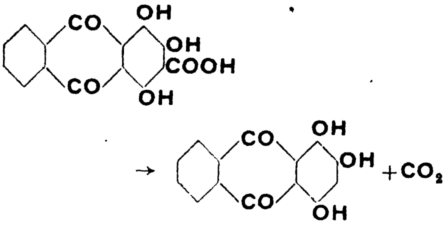
It dissolves in alkalis forming a green solution. Its triacetate melts at 171°–173°. Anthragallol gives the absorption bands : λ=574·5, *525·6*, 486·4, 456·6 in H_2SO_4. Anthragallol is one of the most valuable wool colours. It is used with a chrome or aluminium mordant.

With an excess of ammonia anthragallol reacts to form *anthragallolamide*, or 1-amino-2 : 3-dihydroxyanthraquinone.

On methylating with dimethyl sulphate in boiling nitrobenzene solution containing suspended sodium carbonate, anthragallol gives a *dimethyl ether*, which forms orange needles, m.p. 159°–160°, and which forms an *acetyl* derivative, m.p. 167°. The dimethyl ether is hydrolysed by concentrated sulphuric acid at 100° to give a *monomethyl ether*, m.p. 233° (*acetyl* derivative, m.p. 184°). Methylation with a large excess of dimethyl sulphate and sodium carbonate at 180° converts both the mono- and the dimethyl ethers into a *trimethyl ether*, which is lemon-yellow and melts at 168°.

Literature.—Seuberlich, Ber. 1877, **10**, 39.

Purpurin, 1 : 2 : 4-Trihydroxyanthraquinone.—Purpurin is readily obtained from madder root, which contains a glycoside of *pseudo*-purpurin (purpurin-3-carboxylic acid). This substance, on boiling with alum, is slowly decarboxylated to give purpurin. The purpurin may be separated from the alizarin which is also present in madder extracts by crystallisation from a hot solution of alum, in which the purpurin is more soluble, or by dissolving the mixture in caustic soda and passing carbon dioxide into the solution. This precipitates the alizarin, but not the purpurin.



Purpurin is manufactured by heating 1 part of alizarin with 1 part of pyrolusite in 8–10 parts of sulphuric acid at 160°. Alizarin is also oxidised to purpurin by sulphuric acid alone at 225°, or by ammonium persulphate and oleum.

4-Aminoalizarin is converted into purpurin by nitrous acid in sulphuric acid solution, or by sulphuric acid alone at 150°. Alizarin-3-sulphonic acid is oxidised on heating with sulphuric acid and sodium nitrate to purpurinsulphonic acid, which yields purpurin when heated under pressure with dilute sulphuric acid. A purpurinsulphonic acid is also obtained when anthraquinone-1-sulphonic acid is heated with oleum and the resulting sulphuric acid ether is hydrolysed.

Purpurin crystallises from dilute alcohol in long orange-coloured needles, which contain $1 H_2O$. The pure substance begins to sublime at 150°, and melts at 257°. It is slightly soluble in water, in which it gives a deep yellow solution ; in alkaline carbonates it gives a red colour, in alkalis a purple-red. The solution in alkalis rapidly oxidises in the air, especially in the light. Purpurin dissolves readily in ether, carbon disulphide, benzene or acetic acid.

Absorption spectra : λ=*546·7*, 508·9, 477·7 in **KOH** ; 521·1, *485·5*, 455·5 in alcohol ; 558·5, *512·0*, 478·9 in H_2SO_4 and B_2O_3.

Purpurin is sold in a 20% paste as a mordant dye. It colours chromed cloth a red-brown, and gives on alumina a scarlet-red, which is less fast to light than Turkey Red. Purpurin is used in the manufacture of Alizarin Blue Black and in the preparation of leucoquinizarin by reduction.

When boiled with acetic anhydride purpurin yields a triacetate which crystallises in yellow needles, m.p. 192°–193°. Aqueous ammonia at 150° converts purpurin into 1 : 3-dihydroxy-4-aminoanthraquinone (*purpurinamide*), which, when boiled with ethyl nitrite, yields purpuroxanthin (1 : 3).

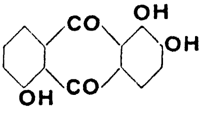
Purpuroxanthin is also the product when purpurin is reduced with either alkaline stannous chloride or sodium amalgam. If, however, zinc-dust be employed as the reducing agent in weakly alkaline, neutral or acid solution, then the leuco-compound of quinizarin (1 : 4) is obtained. Purpurin is converted into an anilino-dihydroxyanthraquinone when heated with a mixture of aniline and aniline hydrochloride. A certain amount of dianilino-hydroxyanthraquinone is produced at the same time.

Purpurin-3 : 8-*disulphonic acid* is obtained by heating the potassium salt of anthraquinone-1 : 5-disulphonic acid with boric acid and 40% oleum under 6–7 atmospheres pressure.

3-*Chloropurpurin* is formed, together with dichloropurpuroxanthin, by the action of sulphuryl chloride on a sulphuric acid solution of 2 : 4-dihydroxybenzoylbenzoic acid in the presence of boric acid. It crystallises in deep red needles melting at 270°–273°.

Literature.—Mettler, Ber. 1912, **45**, 800 ; Marshall, J.C.S. 1931, 3206 ; Hill, Nature, 1934, Oct. 20, 628.

Hydroxyanthrarufin (1 : 2 : 5), Alizarin Brilliant Bordeaux R.—This substance is manufactured by the Bohn-Schmidt reaction from alizarin, or by oxidative alkali fusion from anthraquinone-1 : 5-disulphonic acid.

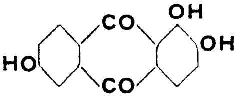


It is also obtained by heating anthrarufin with a mixture of sodium and potassium hydroxides at 180°–185° in the presence of sodium nitrate and water.

Hydroxyanthrarufin crystallises from acetic acid in red needles, m.p. given as 273°–274° and 278° by different investigators. Absorption spectra : λ=619·5, *573·2*, 533·5 in **KOH** ; *636·0* 582·5, 505·8 in H_2SO_4. It is a valuable mordant dyestuff and colours chromed cotton a blue-violet, and purple on an alumina mordant.

Literature.—Liebermann and Dehnst, Ber. 1879, **12**, 1289 ; Liebermann and Boeck, Ber. 1878, **11**, 1716 ; Ziegler, J. pr. Chem. 1912, **86**, 297 ; D.R.P. 195028, 196980, 156960.

Flavopurpurin, 1:2:6-Trihydroxyanthraquinone, Alizarin SDG, G, RG, GI, VG.—Flavopurpurin is the main constituent of the yellow shades of commercial artificial alizarin.



It is an important mordant dyestuff, and is manufactured by the oxidative alkali fusion of anthraquinone-2 : 6-disulphonic acid. The technical details of this process are discussed below under *Anthrapurpurin.*

It is not easy to isolate pure flavopurpurin from commercial artificial alizarin, as this generally contains anthrapurpurin (1 : 2 : 7), which is closely similar to flavopurpurin in chemical properties.

Schmidt's conclusion, which is widely quoted, that anthraflavin (2 : 6) is not formed as an intermediate in the production of flavopurpurin by oxidative alkali fusion of anthraquinone-2 : 6-disulphonic acid has been shown to be incorrect.

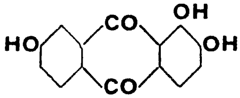
Flavopurpurin has been obtained by condensing hemipinic anhydride with anisole in the presence of aluminium chloride, followed by ring-closure in sulphuric acid solution and demethylation.

Flavopurpurin crystallises from alcohol, in which it is readily soluble in the cold, in anhydrous yellow needles, which do not melt below 360°. It is sparingly soluble in water. It gives a triacetate, m.p. 238°, on heating with acetic anhydride. By direct methylation it gives a dimethyl ether. The trimethyl ether can be obtained by methylating deoxyflavopurpurin and oxidising the product.

The colours given by flavopurpurin on mordanted fabrics are similar to those of alizarin, but the red and brown shades are yellower. It gives a bright yellowish-orange on a tin mordant.

Literature.—Caro, Ber. 1876, **9**, 682 ; Schunck and Römer, Ber. 1876, **9**, 679 ; 1877, **10**, 1823 ; 1880, **13**, 42 ; Bistrzycki and Yssel de Schepper, Ber. 1898, **31**, 2798 ; Graebe, Ber. 1905, **38**, 152 ; D.R.P. 205097, 223103.

Anthrapurpurin, *iso*Purpurin, 1 : 2 : 7-Trihydroxyanthraquinone, Alizarin GD.—This valuable colouring matter is a constituent of the yellow shades of artificial alizarin. It is formed by the oxidative alkali fusion of anthraquinone-2 : 7-disulphonic acid.



The manufacture of alizarin from anthraquinone-2-sulphonic acid always implies the production of a certain amount of the 2 : 6- and 2 : 7-disulphonic acids ; the isolation of these substances has been described in Sec. 6. On fusing with alkali it is possible to obtain from these sulphonic acids either the corresponding dihydroxyanthraquinones, anthraflavin (2 : 6) and *iso*anthraflavin (2 : 7), or, on the other hand, to imitate the alizarin fusion and introduce a further hydroxyl group. In this way anthrapurpurin and flavopurpurin are produced on a commercial scale.

The conversion of anthraflavin and *iso*anthraflavin into the trihydroxyanthraquinones occurs with different rapidity, the former substance reacting more slowly. The reaction takes place when 100 parts of anthraflavin are fused with 50 parts of saltpetre and 1,500 volumes of caustic lye (b.p. 185°) at 215°–225°. In fusing the disulphonic acids with alkali, however, it is probable that when the necessary temperature is reached quickly the reaction leads first to the formation of a certain proportion of alizarinsulphonic acids, which are subsequently changed to flavopurpurin and anthrapurpurin. The following example of the proportions used in the fusion may be given :

2,000 litres of disulphonic acids liquor (obtained as described in Sec. 6) containing solid in suspension and with a dry content of 27·65%, equivalent to 553 kg. of the sodium salts, is mixed with 180 kg. saltpetre and 1,012 litres of soda lye of 45°Bé. (containing 618 kg. NaOH). This mixture is heated nearly to boiling, and three drums of solid caustic soda (795 kg.) are then added. This procedure ensures the rapid heating of the mixture, which is necessary to obtain good results. The reaction is carried out in apparatus similar to that used for the preparation of alizarin, and the fusion takes 48 hours.

The product is worked up in much the same way as alizarin, and is brought into commerce in the form of a paste. Anthraflavin is usually present as an impurity in these trihydroxyanthraquinones, and may be separated by diluting the melt to 10°–12°Bé., when the insoluble sodium salt of anthraflavin separates and may be filtered off.

Anthrapurpurin can be isolated, with some difficulty, from the mixture of hydroxyanthraquinones in crude artificial alizarin by treating their alumina lakes with sodium carbonate, in which the anthrapurpurin lake dissolves, leaving the alizarin lake unattacked. The anthrapurpurin is then further purified by converting it into its sparingly soluble sodium salt and precipitating the barium salt.

Anthrapurpurin is formed when *m*-benzdioxyanthraquinone (1 : 7) or α-dibromoanthraquinone is fused with potash.

Anthrapurpurin crystallises from acetic acid in orange-coloured needles which melt above 360° and sublime in long red needles. It dissolves in alkalis with a violet colour. Absorption spectra : λ=605·8, 651·8, 523·0 in KOH ; 548·5, 508·8, 478·3 in H_2SO_4. With acetic anhydride it forms a triacetate, yellow needles, m.p. 220°.

Anthrapurpurin is similar to alizarin in dyeing properties and gives reds, purples, and blacks on alumina, chrome, and iron mordants respectively ; but the reds are much purer and less blue than those of alizarin, while the purples are bluer and the blacks more intense. When used in Turkey Red dyeing, it gives a very brilliant scarlet, which is of remarkable permanence.

When heated with ammonia, *anthrapurpurinamide*, $C_{14}H_5O_2(NH_2)(OH)_2$, is formed.

Literature.—Perkin, J.C.S. 1872, **25**, 659 ; 1873, **26**, 425 ; Caro, Ber. 1876, **9**, 682 ; Schunck and Römer, Ber. 1876, **9**, 679 ; 1877, **10**, 972, 1823 ; 1880, **13**, 42 ; Auerbach, Jahresber. 1874, 488 ; D.R.P. 194945, 205097, 223103.

Hydroxychrysazin, 1 : 2 : 8-Trihydroxyanthraquinone.—This substance is obtained from chrysazin (1 : 8) by the Bohn-Schmidt reaction, or by fusing with aqueous potassium hydroxide and sodium nitrate at 180°–185°.

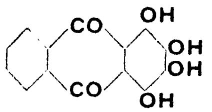
It crystallises in orange needles, m.p. 239°, and forms a triacetyl-derivative, m.p. 219°. The trimethyl ether forms yellow needles, m.p. 157°. Hydroxychrysazin is not used as a colouring matter but as an intermediate in the preparation of Alizarin Brilliant Cyanine Green.

1 : 3 : 8-Trihydroxyanthraquinone is obtained from *rhein* through its amide and dihydroxyaminoanthraquinone. It melts at 277°–278° and gives a triacetyl derivative, m.p. 197°–198° (Oesterle, Arch. Pharm. 1912, **250**, 301).

1 : 4 : 6-Trihydroxyanthraquinone is the chief product when 4-amino-phthalic anhydride and quinol are heated with sulphuric acid at 170°–190°.

1 : 4 : 8-Trihydroxyanthraquinone is obtained from chrysazin by the Bohn-Schmidt reaction, using 80% oleum and a temperature of 25°–35°. The sulphuric acid ester so formed is hydrolysed by heating with 98% sulphuric acid, the product crystallises from pyridine in brown-red needles with a green metallic glance. It gives violet solutions in sodium hydroxide and in sulphuric acid. It is also obtained by reducing Alizarin Bordeaux (1 : 2 : 5 : 8) (D.R.P. 161026).

16. TETRAHYDROXYANTHRAQUINONES.



1 : 2 : 3 : 4-Tetrahydroxyanthraquinone is obtained by heating anthragallol with sulphuric acid and boric acid at 200°–240°. It forms green needles, soluble in both alkalis and sulphuric acid with a red colour. The tetra-acetyl derivative melts at 205° (D.R.P. 86968).

a-Hydroxyanthragallol, β-Hydroxyanthragallol.—A mixture of 1 : 2 : 3 : 5- and 1 : 2 : 3 : 7-tetrahydroxyanthraquinones (*a*- and *β*-hydroxyanthragallols respectively) is obtained by heating equimolecular proportions of gallic acid and *m*-hydroxybenzoic acid with 10 parts of sulphuric acid at 150° for 20 hours. The precipitate obtained by pouring the product into water is extracted with alcohol, and the residue obtained on evaporation is treated with hot benzene. The *a*-compound passes into solution leaving the *β*-compound undissolved.

The *a*-compound crystallises in golden-yellow micro-needles from alcohol. It gives a green solution in alkalis, and a red solution in sulphuric acid. Its tetra-acetyl derivative melts at 207°–209°.

β-Hydroxyanthragallol crystallises from alcohol in red needles. It gives a brown-red solution in sulphuric acid. Its tetra-acetate forms lemon-yellow plates, m.p. 189°.

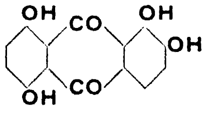
Literature.—Noah, Annalen, 1887, **241**, 270.

Rufiopin, 1 : 2 : 5 : 6-Tetrahydroxyanthraquinone.—This substance is obtained by heating opianic or hemipinic acid with sulphuric acid at 180°, or by fusing anthrarufin disulphonic acid with potash. It forms an orange-coloured crust from ether and can be sublimed in orange needles.

It gives a violet-red solution in alkalis and also in sulphuric acid. It forms only dull brown shades with mordants, and is of no value as a dyestuff.

Literature.—Liebermann and Chojnacki, Annalen, 1872, **162**, 323 ; D.R.P. 103988.

Quinalizarin, Alizarin Bordeaux, 1 : 2 : 5 : 8-Tetrahydroxyanthraquinone.—Quinalizarin is obtained in almost quantitative yield by treating alizarin with 80% oleum for 3–4 days at 40°–50°. This gives the sulphuric acid ester of quinalizarin, which forms quinalizarin on hydrolysis by boiling with hydrochloric acid.



It has also been prepared by condensing hemipinic acid with quinol in sulphuric acid solution, and demethylating the resulting dimethyl ether.

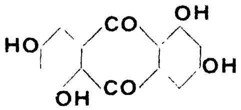
Quinalizarin can be obtained in deep red needles with green metallic glance. Absorption spectra : λ=*587·0*, 543·5 in **KOH** ; 530·7, 517·0, *490·2*, 461·4 in alcohol ; 637·7, *573·2*, 530·3, 492·0 in H_2SO_4 ; 635·4, *590·9* in H_2SO_4 and B_2O_3. The tetra-acetate crystallises from alcohol-chloroform mixture in micro-needles, m.p. 201°.

Quinalizarin gives on an alumina mordant Bordeaux Red, on iron and chromium a violet-red. The colours are very fast to light, soap, and acids.

The name "Bordeaux" is used in commerce as a collective term to describe a number of mixtures of hydroxyanthraquinones obtained by the Bohn-Schmidt reaction, and having similar dyeing properties to quinalizarin.

Literature.—Schmidt, J. pr. Chem. 1891 [ii], **43**, 239 ; Liebermann and Wense, Annalen, 1887, **240**, 299.

Anthrachrysone, 1 : 3 : 5 : 7-Tetrahydroxyanthraquinone.—Anthrachrysone is readily obtained by heating one part of 3 : 5-dihydroxybenzoic acid with ten parts of sulphuric acid for three to five hours.



It crystallises from alcohol in silky needles and sublimes with partial decomposition in yellow leaflets, which melt above 360°. Absorption spectra : λ=504·8, 472·0 in H_2SO_4 ; 512·8, 478·3 in H_2SO_4 and B_2O_3. The tetra-acetyl derivative crystallises in yellow needles from acetic acid, m.p. 253°.

Anthrachrysone has very little affinity for mordants. The solution in 33% sodium hydroxide deposits a bright red sodium salt, which is converted into an ammonium salt by ammonium chloride. Anthrachrysone dimethyl ether is formed when the potassium salt is heated with dimethyl sulphate at 180°–190° ; it crystallises in golden-brown columns from nitrobenzene. A small amount of the tetramethyl ether is formed at the same time, it crystallises in golden-yellow prisms, m.p. 294°.

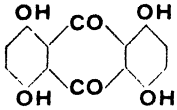
When heated with an excess of oleum, *anthrachrysone*-2 : 6-*disulphonic acid* is obtained (D.R.P. 70803). It forms a characteristic sodium salt which crystallises in glistening coppery platelets and forms 2 : 6-*dichloroanthrachrysone* by displacement of the sulphonic acid groups on treatment with sodium hypochlorite.

The bromination of anthrachrysone in acetic acid solution gives a *dibromoanthrachrysone*, which forms orange-red needles, m.p. above 290°. The bromination of the disulphonic acid in dilute acetic acid solution gives a *tetrabromoanthrachrysone*, which forms dark red needles, m.p. above 300°.

Anthrachrysone is readily converted into Acid Alizarin Blue BB and Acid Alizarin Green (*see* Sec. 21).

Literature.—Hohenemser, Ber. 1902, **35**, 2305 ; Noal, Ber. 1886, **19**, 755 ; Fischer and Ziegler, J. pr. Chem. 1912 [ii], **86**, 297 ; Barth and Senhofer, Annalen, 1872, **164**, 109.

1 : 4 : 5 : 8-Tetrahydroxyanthraquinone.



—This substance has been obtained by the action of sulphuric acid on 4 : 8-dinitroanthrarufin. It can be prepared by heating 5 : 8-dichloroquinizarin for 20 hours at 250° under pressure with copper powder and milk of lime.

It crystallises in brown needles from a mixture of benzene and ligroin ; m.p. 246°. Absorption spectrum : λ= 636·4, 617·1, 584·2, 567·5, 539·9, 526·2 in H_2SO_4. It dissolves with a cornflower-blue colour in alkalis. The tetra-acetyl derivative forms light yellow needles which melt with decomposition at 250°. A tetramethyl ether is formed when the sparingly soluble blue potassium salt is heated with dimethyl sulphate at 180° ; it forms lustrous orange leaflets, m.p. 317°.

It is of interest that this tetrahydroxyanthraquinone has the properties of a powerful mordant dyestuff.

Literature.—Fischer and Ziegler, J. pr. Chem. 1912 [ii], **86**, 297 ; Frey, Ber. 1912, **45**, 1361 ; D.R.P. 125579, 162033.

Dihydroxychrysazins.—Two isomeric dihydroxychrysazins have been obtained from chrysazin. The first, obtained by fusing chrysazin with potassium hydroxide, forms dark red needles, m.p. 217°, sublimes *in vacuo*, and gives colours with mordants (Schrubsdorff, Ber. 1902, **35**, 2936). The second, obtained by fusing chrysazin-disulphonic acid with alkali, melts at 292°, colours mordants, and gives a tetra-acetyl derivative, m.p. 233° (Wölbling, Ber. 1903, **36**, 2941).

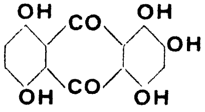
17. POLYHYDROXYANTHRAQUINONES.

Dihydroxyanthragallol.—1 : 2 : 3 : 5 : 7-Pentahydroxyanthraquinone has been prepared by heating equal parts of gallic acid and 3 : 5-dihydroxy-benzoic acid with ten parts of sulphuric acid for 10 minutes at 160°. The product, containing anthrachrysone (1 : 3 : 5 : 7), rufigallol (1 : 2 : 3 : 5 : 6 : 7), and dihydroxyanthragallol, is treated with acetic anhydride, and the acetyl derivatives are separated by treatment with alcohol, in which only the acetyl derivative of dihydroxyanthragallol dissolves. The acetyl derivative so obtained, m.p. 229°, is hydrolysed by means of dilute sulphuric acid to give dihydroxyanthragallol, it crystallises from alcohol in small red needles which do not melt at 360°.

The substance is similar to rufigallol in tinctorial properties.

Literature.—Noah, Annalen, 1887, **241**, 275.

Alizarin Cyanine R, Alizarin Pentacyanin.—1 : 2 : 4 : 5 : 8-Pentahydroxyanthraquinone is obtained by oxidising quinalizarin with manganese dioxide in sulphuric acid solution. The sulphuric acid ester obtained in this way is hydrolysed by boiling with dilute acid, and the resulting Alizarin Cyanine R may be crystallised from nitrobenzene in bronze-coloured leaflets.



It gives a blue solution with red fluorescence in sulphuric acid and yields a blue chromium lake. Absorption spectra, λ=*581·9*, 538·7, 502·4 in **KOH** ; *633·2*, 583·0, 538·5, in H_2SO_4.

Rufigallol, Rufigallic Acid.—1 : 2 : 3 : 5 : 6 : 7-Hexahydroxyanthraquinone may be obtained by heating gallic acid with sulphuric acid at 140°. It sublimes in yellow needles, gives a violet solution in alkalis and red in sulphuric acid and yields a blue precipitate with barium hydroxide.

The colours produced on alumina, iron, and chromium mordants are red, violet and brown respectively, but they are not pure in tone.

Alizarin is formed when rufigallol is reduced with sodium amalgam.

Anthracene Blue and Alizarin Hexacyanine, which are **1 : 2 : 4 : 5 : 6 : 8-** and **1 : 2 : 4 : 5 : 7 : 8-hexahydroxyanthraquinones** respectively, are formed as the main end-products when the Bohn-Schmidt reaction is applied to almost any of the hydroxyanthraquinones.

They give Marine Blue on wool mordanted with chromium, and are the main constituents of a number of brands of "Alizarin Cyanine Blues." They are less fast to light than the alizarin quinoline blues but are cheaper, faster to rubbing and more level-dyeing and, consequently, have replaced the alizarin quinoline blues to a considerable extent.

Anthracene Blue may be obtained by treating 1 : 5-dinitroanthraquinone with 40% oleum and sulphur, and hydrolysis of the product with ordinary sulphuric acid. It gives a violet-blue solution with brown fluorescence in sulphuric acid. Absorption spectra: λ=*603·0*, 588·3, *555·9*, 542·5, 513·6 in H_2SO_4 ; *599·7*, 550·7, 506·4 in H_2SO_4 and B_2O_3. The aluminium lake is violet, the chromium lake blue.

The disulphonic acid of Anthracene Blue is *Acid Alizarin Blue BB*.

Literature.—Schmidt, J. Soc. Dyers and Col. 1919, **35**, 216.

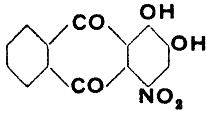
MORDANT DYESTUFFS DERIVED FROM ALIZARIN.

18. NITRO-HYDROXYANTHRAQUINONES.

The nitro-hydroxyanthraquinones are mainly important as intermediates in the production of the aminohydroxyanthraquinones and the anthraquinone quinolines, many of which are valuable dyestuffs.

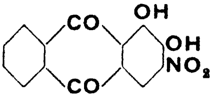
They are easily obtained by the nitration of the hydroxyanthraquinones, and are generally prepared in this way. The position occupied by an entering nitro-group may be determined to a considerable extent by careful control of the conditions of nitration, by the adjustment of such factors as the solvent used, the strength of nitric acid, the temperature of nitration, and by the addition of boric acid.

4-Nitroalizarin (α-Nitroalizarin), Alizarin Brown.—4-Nitroalizarin is manufactured by adding the calculated quantity of nitric acid, dissolved in sulphuric acid, to a solution of alizarin in sulphuric acid at −5° to −10°.



It crystallises from alcohol or acetic acid in golden-yellow needles, m.p. 194°–196°. It was formerly used as a mordant dyestuff. On warming with sulphuric acid it forms 1 : 2 : 3 : 4-tetrahydroxyanthraquinone.

3-Nitroalizarin (β-Nitroalizarin), Alizarin Orange is manufactured by nitrating a solution of alizarin in toluene or in sulphuric acid with 66% nitric acid. Boric acid is generally added to the mixture. It may also be prepared by boiling 1 : 3-dinitro-2-hydroxyanthraquinone with 20% caustic soda solution.



3-Nitroalizarin crystallises from acetic acid in orange-yellow needles which melt with partial decomposition at 244° and sublime with decomposition at a higher temperature. With benzoyl chloride it gives a dibenzoyl derivative, m.p. 252°.

On cloth mordanted with alumina it gives a good orange, with tin a reddish-orange, with copper a reddish-brown, and with chromium a brown-red.

Literature.—Rosenstiehl, Bull. Soc. chim. 1901, **26**, 63 ; Schunck and Römer, Ber. 1879, **12**, 584 ; Simon, Ber. 1882, **15**, 692 ; Barnes, J. Soc. Dyers and Col. 1899, **15** (I), 11 ; D.R.P. 74562.

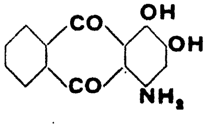
Alizarin Orange G, 3-Nitroflavopurpurin, is prepared by nitrating flavopurpurin (1 : 2 : 6). It was formerly used as a mordant dyestuff.

2 : 4 : 5 : 7-Tetranitrochrysazin is very easily prepared by the action of nitric acid on aloes. It is of interest since the nitro-groups are so mobile that they react with aromatic amines in aqueous soda solution.

Alizarin Cyanine Black G, 3-Nitro-1 : 2 : 4 : 5 : 7 : 8-hexahydroxyanthraquinone, is prepared by hydroxylating 3-nitro-anthrapurpurin with oleum and manganese dioxide. It gives a fast black on a chromium mordant (Schmidt, J.S.C.I. 1914, **33**, 1040).

19. AMINOHYDROXYANTHRAQUINONE MORDANT DYESTUFFS.

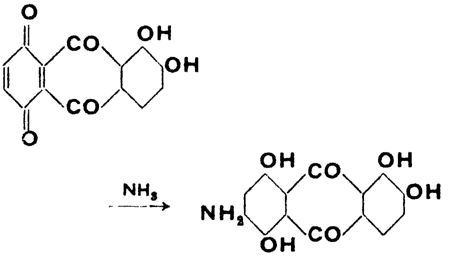
Alizarin Garnet, Alizarin Cardinal, 4-Aminoalizarin.—This valuable dyestuff, which is obtained by reducing 4-nitroalizarin, crystallises from alcohol in small black needles with metallic lustre.



It is much used in calico-printing. It gives a purple colour with an alumina mordant, and a bluish colour on iron. With boiling acetic anhydride it gives a diacetyl derivative, m.p. 245°.

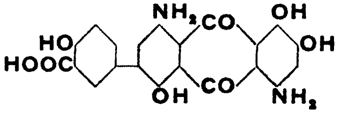
Alizarin Maroon, 3-Aminoalizarin.—This substance is obtained by reducing 3-nitroalizarin. It gives a red colour on alumina, but is not much used now as a dyestuff.

Alizarin Cyanine G, 6-Amino-1 : 2 : 5 : 8-tetrahydroxyanthraquinone.—This substance is prepared technically by the addition of ammonia to the anthra*di*quinone, which is obtained by oxidising quinalizarin with manganese dioxide in sulphuric acid solution. (An alternative formulation is given in the "Colour Index," Soc. Dyers and Col. 1924, No. 1051). It gives a greener blue than Alizarin Cyanine R on a chromium mordant.



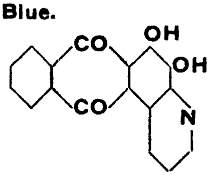
The name "Alizarin Cyanine" is given to a number of brands of dyestuffs which are for the most part mixtures of aminohydroxyanthraquinones obtained by heating the polyhydroxyanthraquinones with ammonia.

Alizarin Brilliant Cyanine GG.—This is one of the most valuable of the Alizarin Cyanine colours. It is prepared technically by condensing the diquinone of quinalizarin with salicylic acid, and treating the product with ammonia. The formula shown is given by Fierz-David, "Künstliche Organische Farbstoffe," 1926.



20. ALIZARIN QUINOLINES.

Alizarin Blue.

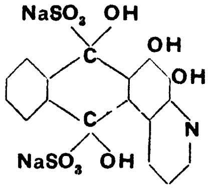


This valuable dyestuff is prepared technically by adding glycerol very slowly to a mixture of 3-aminoalizarin and 3-nitroalizarin in sulphuric acid solution. Its chemical constitution was first demonstrated by Graebe, who showed that it is a quinoline derivative of alizarin.

Alizarin blue crystallises from benzene in brownish-violet needles, m.p. 270°, which sublime at a high temperature. It is insoluble in water, sparingly soluble in alcohol and ether, more easily soluble in hot benzene. It dissolves in ammonia and caustic alkalis to give blue solutions. It also has basic properties and gives salts with acids.

The hydrochloride separates as a red crystalline precipitate, $C_{17}H_9NO_4,HCl$, when hydrogen chloride is passed into a solution of Alizarin Blue in boiling benzene.

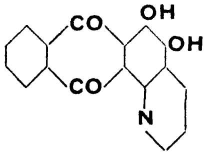
Alizarin Blue ABS (*B.A.C.*), the bisulphite-compound of Alizarin Blue, is manufactured on a large scale and is particularly suitable for calico-printing as it is soluble in water.



The Alizarin Blues are generally used for dyeing cotton or wool with a chromium mordant, but they may also be used for dyeing silk with an alumina or iron mordant.

Literature.—Prud'homme, Bull. Soc. chim. 1902, **28**, 62 ; Graebe, Annalen, 1880, **201**, 333 ; Auerbach, J.C.S. 1879, **35**, 800 ; Prud'homme and Rabaut, Bull. Soc. Ind. Mulhouse, 1893, 223.

Alizarin Green.



This dyestuff is the alizarin quinoline which is obtained when 4-aminoalizarin is treated with glycerol in sulphuric acid solution. Its properties resemble Alizarin Blue, and its bisulphite compound, *Alizarin Green S*, is used with a nickel-magnesia mordant in calico printing.

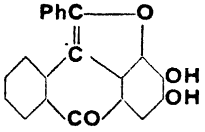
Alizarin Black P is the quinoline derived from 3-nitroflavopurpurin (3-nitro-1 : 2 : 6-trihydroxyanthraquinone). Its bisulphite compound, *Alizarin Black S*, is used in calico printing to produce a fast violet-grey or black.

Alizarin Green X is obtained by treating Alizarin Blue first with fuming sulphuric acid, and then with ordinary sulphuric acid. It is mainly a sulphonic acid of a hydroxy-derivative of Alizarin Blue, and is much used in calico printing with a chromium mordant.

Alizarin Indigo Blue S (B.A.S.F.) is the bisulphite compound of a dyestuff obtained by oxidising Alizarin Blue with 80% oleum. It is a mixture of 5 : 8-dihydroxy- and 5 : 6 : 8-trihydroxy-derivatives of Alizarin Blue.

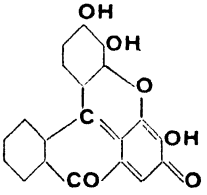
Benzoin Yellow and Cœrulein may be mentioned here as hydroxyanthraquinone derivatives containing heterocyclic rings.

Benzoin Yellow is a mordant dyestuff that gives a fast yellow coloration on a chromium mordant.



It may be prepared by condensing benzoin with gallic acid in sulphuric acid solution, but it is no longer used owing to its high cost.

Cœrulein is obtained from Gallein, which is the condensation product of one molecule of phthalic anhydride with two molecules of pyrogallol.



Gallein itself possesses mordant dyeing properties, and gives cœrulein when heated with 20 parts of sulphuric acid at 200°, which forms a bluish-black mass with a metallic lustre, almost insoluble in water, ether and alcohol, but dissolving more readily in acetic acid. It dissolves with a green colour in alkalis and with an olive-brown colour in acids. With acetic anhydride it forms a triacetate.

When treated with sodium bisulphite it forms a soluble bisulphite compound, *Cœrulein S*, which is used in calico printing, giving with each type of mordant very fast olive-green shades.

Cœrulein B is obtained by heating fluorescein in oleum solution. It colours chromium mordanted cloth a fast blue.

Literature.—Baeyer, Ber. 1871, **4**, 556, 663 ; Orndorff and Brewer, Amer. Chem. Journ. 1901, 97 ; King, J.C.S. 1934, 1064.

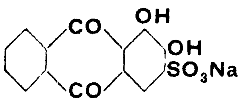
ACID WOOL DYES.

21. **Hydroxyanthraquinone - Sulphonic Acids.**—Many of the sulphonic acid derivatives of the hydroxyanthraquinones are valuable acid wool dyes. A number of them have also mordant dyeing properties, and can be applied to a mordanted cloth or can be after-chromed.

These substances are prepared in general by direct sulphonation of the hydroxyanthraquinones ; the use of mercury salts and of boric acid plays an important part in the sulphonations. To a lesser extent they are obtained by the hydroxylation of anthraquinone sulphonic acids, or by the partial replacement of sulphonic acid groups by hydroxyl.

Besides sulphonation with sulphuric acid, sulphonic acid groups can sometimes be introduced by heating with aqueous sodium sulphite and an oxidising agent. Quinizarin, for example, gives the 2-sulphonic acid in quantitative yield, when heated with aqueous sodium sulphite and copper oxide.

Alizarin Red S, WS (M.L.B.), Alizarin Powder W (By.).



Alizarin Red, the sodium salt of alizarin-3-sulphonic acid, is easily obtained by the direct sulphonation of alizarin. It gives brilliant scarlet-red shades with an alumina mordant, and Bordeaux red shades on chromium. The sulphonic acid group makes it much more soluble than alizarin, and it is very level-dyeing. It is manufactured in very large quantities for dyeing woollen goods.

Like many hydroxyanthraquinone derivatives, this substance is used as an indicator. The colour change occurs between p_H 3·7 (yellow) and 4·2 (pink).

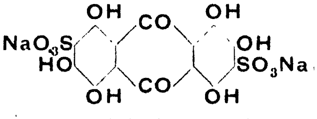
Literature.—Graebe and Liebermann, Annalen, 1871, **160**, 144 ; Walpole, J.S.C.I. 1915, **34**, 153.

Alizarin-3:5- and 3:8-Disulphonic Acids are obtained together by disulphonating alizarin in the presence of mercuric sulphate. The 3 : 5-disulphonic acid is also obtained, together with quinizarin-α-sulphonic acid, by heating anthraquinone-1-sulphonic acid with 40% oleum and boric acid at 130°–135°.

Erweco Acid Alizarin Red BS is a mixture of the sodium salts of alizarin-5- and 8-sulphonic acids, manufactured by eliminating the 3-sulphonic acid groups from the mixture of 3 : 5- and 3 : 8-disulphonic acids which is obtained by sulphonating alizarin in the presence of mercuric sulphate. The elimination is effected by heating with 80% sulphuric acid (D.R.P. 210863).

Alizarin Red 3WS is sodium flavopurpurin-3-sulphonate.

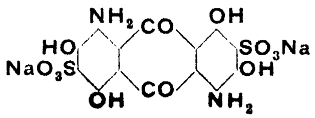
Acid Alizarin Blue BB, Alizarin Cyanin WRS, Anthracene Blue SWX.—This dyestuff, which is the sodium salt of the disulphonic acid of Anthracene Blue, may be obtained by boiling 4 : 8 - diamino - anthrachrysone - disulphonic acid with alkali. It is manufactured by heating 1 : 5-dinitroanthraquinone with a mixture of oleum, sulphur and boric anhydride at 130°. The quinone-imine so formed is hydrolysed with water, and the resulting anthradiquinone reduced with sulphur dioxide.



It produces a red shade on wool from an acid bath and on after-chroming develops a beautiful blue, exceedingly fast to milling, acids and alkalis.

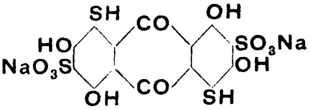
Literature.—Fierz-David, "Künstliche Organische Farbstoffe," 1926.

Acid Alizarin Blue GR is obtained by warming Acid Alizarin Blue BB with 5% ammonia, or from anthrachrysone by successive nitration, sulphonation and reduction.

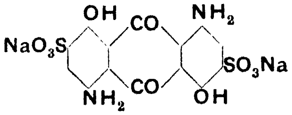


Literature.—D.R.P. 115082, 119756, 105567.

Acid Alizarin Green B, G, is obtained by reducing dinitro - anthrachrysone - disulphonic acid with alkaline sodium sulphide.

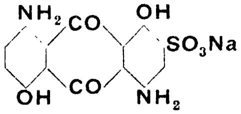


Alizarin Saphirol B, Solway Blue, Alizarin Delphinol.—This valuable acid dye is obtained from anthrarufin (1 : 5) by successive sulphonation, nitration and reduction. It may also be obtained from 1 : 5-dinitroanthraquinone by reduction in alkaline solution, followed by sulphonation.



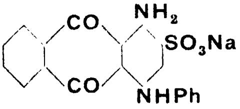
It dyes wool a blue shade which becomes more violet on after-chroming. It is very level-dyeing and extremely fast.

Alizarin Saphirol SE, Alizarin Delphinol SEN is obtained from Alizarin Saphirol B by reducing it to the leuco-compound and eliminating one sulphonic acid group (D.R.P. 108578, 110880, 117892).



Alizarin Celestol is obtained by the action of formaldehyde on Alizarin Saphirol B.

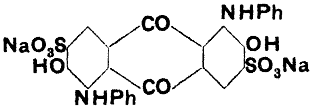
Alizarin Saphirol A is prepared from 1-amino-4-bromoanthraquinone-2-sulphonic acid by condensation with aniline.



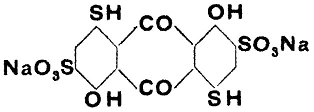
1 - Aminoanthraquinone - 2 - sulphonic acid, which is an intermediate in the manufacture of this dye, is obtained in an interesting manner, by heating the acid sulphate of 1 aminoanthraquinone *in vacuo* to 210°–240°, when rearrangement occurs (D.R.P. 489460).

A series of dyes giving different shades of blues and reds has been obtained by condensing the same bromo-compound with different amines (B.P. 282452, 282469 ; D.R.P. 456114).

Erweco Alizarin Blue R is prepared by condensing 1 : 5 - dinitroanthraflavin - 3 : 7-disulphonic acid with aniline.

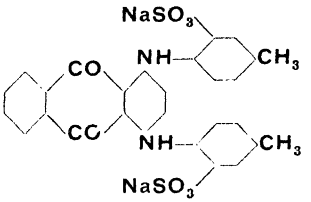


Alizarin Emeraldol G is obtained by reducing dinitroanthrarufin-disulphonic acid with sodium sulphide (D.R.P. 172575, 178840, 180016).



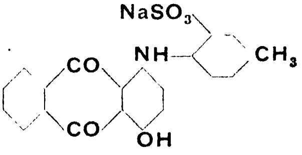
22. Acid Dyes Derived from Quinizarin.

Alizarin Cyanine Green, which was the first of the acid wool dyes to be obtained from quinizarin, may be prepared by boiling a mixture of quinizarin and boric acid in *p*-toluidine and then disulphonating the 1 : 4-ditoluidinoanthraquinone so formed.



Either one or both of the hydroxyl-groups in quinizarin may be replaced by an arylamino-group and a considerable sub-group of anthraquinone dyes has been obtained by sulphonating the products prepared in this way.

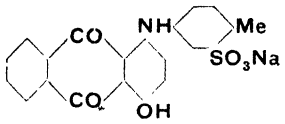
The condensation of quinizarin with *one* molecule of *p*-toluidine, followed by sulphonation, gives **Alizarin Irisol.**



The technical production of these dyes was greatly assisted by the discovery that leucoquinizarin reacts with arylamines much more readily than quinizarin itself. The condensation of *p*-toluidine with leucoquinizarin occurs at 90°. The reaction between quinizarin and arylamines has been shown to be reversible (Friedländer and Schick, Zeit. Textil. Farb. Chem. 1902, **2**, 429 ; 1903, **3**, 218). By condensing leucoquinizarin directly with a toluidine sulphonic acid the subsequent sulphonation can be avoided (D.R.P. 144634).

Quinizarin is generally obtained by the oxidation of anthraquinone with nitrosyl-sulphuric acid ; but it is very difficult to obtain a pure product by this method and, in view of this difficulty, dyes of the Alizarin Cyanine Green type are now generally prepared technically from the easily accessible 1-nitro-4-chloroanthraquinone or 1-nitro-4-hydroxyanthraquinone. Toluidine reacts with 1-nitro-4-hydroxyanthraquinone to give the hydroxy-toluidinoanthraquinone in quantitative yield ; azoxytoluidine is simultaneously formed. 1-Bromo-4-hydroxyanthraquinone is also used as an intermediate in the production of Alizarin Irisols.

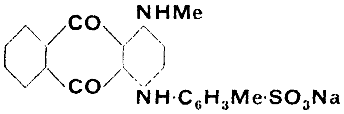
Alizarin Cyanol Violet R is of similar constitution to Alizarin Irisol D, but the sulphonate group occupies the position *meta* to the amino-group.



It is obtained by condensing 4-aminotoluene-2-sulphonic acid with leucoquinizarin, 1-nitro-4-hydroxyanthraquinone, or 1-halogeno-4-hydroxyanthraquinone.

Quinizarin Blue may be obtained by condensing leucoquinizarin with one molecule of aniline and sulphonating the product. From an acid bath it dyes wool a reddish-blue and gives a greenish-blue on chromed wool.

Alizarin Astrol BG is prepared by condensing *p*-toluidine with 1-methylamino-4-hydroxyanthraquinone, 1-methylamino-4-nitroanthraquinone, or 1-methylamino-4-bromoanthraquinone, and sulphonating the product.



The sulphonic group is *ortho* to the amino group. It dyes wool a greenish-blue which is made more fast to milling by after-chroming. It is very level-dyeing, but not extremely fast to light.

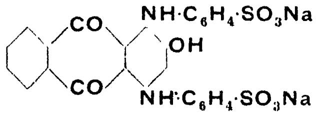
Alizarin Direct Blue differs from Alizarin Astrol only in the position of the sulphonic acid group, which is *meta* to the amino-group.

Alizarin Uranol R is prepared by condensing 1 : 4-diaminoanthraquinone (*see* Sec. 8) with epichlorhydrin and sulphonating the resulting product in which each of the original amino groups is replaced by the group

$$-NH-CH_2-CH(OH)-CH_2Cl$$

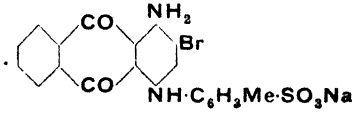
(D.R.P. 218571). The dye which is obtained in a similar manner by condensing the same diamine with ethylene oxide in acetic acid and nitrobenzene solution is known as *Alizarin Uranol 2B* (D.R.P. 235312).

Alizarin Blue-Black 3B, Alizurol Blue-Black (BAC) prepared by condensing purpurin and aniline in the presence of boric acid at 180°–200° and sulphonating. (One of the anilino-sulphonic acid groups may be in the 2-position.)



It is a dye that is used extensively, giving a blue-grey on a chromium mordant that is very fast to light and very level-dyeing.

Alizarin Pure Blue B, Alizarin Sky Blue B is prepared by condensing *p*-toluidine with 1-amino-2 : 4-dibromoanthraquinone (*see* Sec. 5) and sulphonating the product.

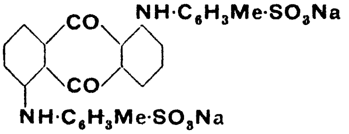


Anthraquinone Blue SR is obtained from 1 : 5-diamino-2 : 4 : 6 : 8-tetrabromoanthraquinone by condensation with *p*-toluidine followed by sulphonation.

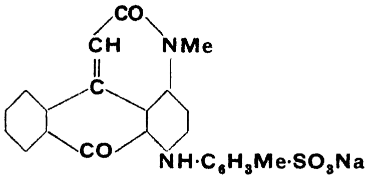
Alizarin Brilliant Green G, SE, is an isomeride of Alizarin Cyanine Green, and is obtained by condensing leucoquinizarin with 4-aminotoluene-2-sulphonic acid. The sodium sulphonate group therefore occupies the position *meta* to the amino-group.

Alizarin Viridine and **Alizarin Brilliant Cyanine Green** are prepared by condensing *p*-toluidine with 1 : 4 : 5-trihydroxyanthraquinone and Alizarin Bordeaux respectively and sulphonating the products.

Anthraquinone Violet is obtained from 1 : 5-dinitro- or 1 : 5-dichloro-anthraquinone by condensing with *p*-toluidine and sulphonating the product (D.R.P. 157123, 205159).

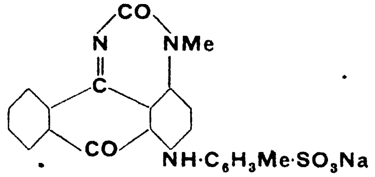


Alizarin Rubinol G is obtained by sulphonating *p*-toluidino-*N*-methyl-anthrapyridone. The pyridone ring is formed when an *N*-acetyl-1-amino-anthraquinone derivative is heated in sulphuric acid.



It dyes wool in red shades from an acid bath (D.R.P. 201904).

Alizarin Geraniol B.



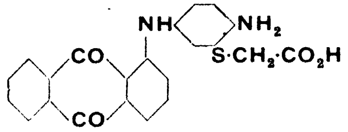
This anthraquinone-pyrimidone dye is obtained from 4-nitro-1-methylaminoanthraquinone. The condensation product with *p*-toluidine is treated with urethane, the ring-closure to the pyrimidone effected by means of zinc chloride, and the resulting product sulphonated. It gives a vivid red-violet on wool (D.R.P. 149801, 256515, 156759, 164791, 159129, 205035).

Other dyes of similar constitution are : **Alizarin Cyclamen R ; Cyananthrol ; Alizarin Emeraldol ; Alizarin Heliotrope R, BB ; Alizarin Marine Blue RG ; Alizarin Turquoise ; Alizarin Brilliant Pure Blue R ; Anthraquinone Blue SR ; Alizarin Direct Violet.**

Literature.—D.R.P. 131873, 218571, 235312, 220627, 86150, 91149, 181879, 170173, 151511, 235776, 86539, 159129, 91150, 92591, 84509, 89862, 125698, 126803, 172464, 106227, 108274.

Recent patents describe a large number of similarly constituted acid wool dyes, obtained by condensing halogenoanthraquinones with a variety of different amines. The easily accessible 1-amino-4-bromoanthraquinone-2-sulphonic acid is a commonly used intermediate, and 2 : 3-dihalogeno-1 : 4-diaminoanthraquinones are also coming into use. The amines used include the *p*-alkylaminoacetanilides, *p*-aminophenylglycol ethers, and 4-aminodiphenyl derivatives (B.P. 379630, 383871, 393316, 392056, 412920, 416433, 359348, 381954 ; U.S.P. 1973025).

Anthraquinone-thioglycollic Acid Dyes.—A recent development of exceptional interest is the use of anthraquinone-*o*-aminoaryl-thioglycollic acid derivatives as dyes.



These substances are soluble in water, but form insoluble compounds on the fibre by the closing of the lactam ring. They give dyeings which are very fast to washing, milling and potting (B.P. 377740, 394312, 412920, 406733).

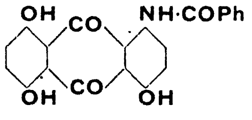
23. ACYLAMINOANTHRAQUINONES.

The acylaminoanthraquinones, which include a number of the *Algol* and *Helindone* colours, form a group of valuable vat dyes which are closely related to the hydroxyanthraquinones (*see* VAT DYES).

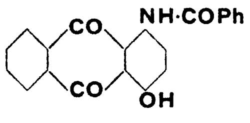
The following are typical examples :

Algol Yellow WG, or 1-benzoylaminoanthraquinone, is obtained by benzoylating 1-aminoanthraquinone.

Algol Violet B may be obtained from Algol Yellow WG by direct hydroxylation. It dyes from a red-brown vat.



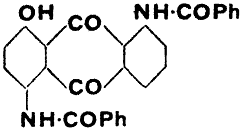
Algol Pink R, 1-benzoylamino-4-hydroxyanthraquinone, is obtained from erythroxyanthraquinone by successive nitration, reduction and benzoylation.



Algol Scarlet, 1-benzoylamino-4-methoxyanthraquinone, is obtained from 1-methoxyanthraquinone by successive nitration, reduction and benzoylation.

Algol Yellow R, *N* : *N'*-dibenzoyl-1 : 5-diaminoanthraquinone, is prepared by benzoylating 1 : 5-diaminoanthraquinone.

Algol Red FF may be obtained from Algol Yellow R by hydroxylation.

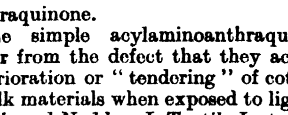


Helio Fast Yellow is 1-salicylaminoanthraquinone.

The simple acylaminoanthraquinone dyes suffer from the defect that they accelerate the deterioration or " tendering " of cotton, viscose or silk materials when exposed to light (Derrett-Smith and Nodder, J. Textile Inst. 1932, **23**, T, 293 ; Whittaker, J. Soc. Dyers and Col. 1933, **49**, 9).

Literature.—Reverdin, Helv. Chim. Acta, 1918, **1**, 209 ; Noelting and Wortmann, Ber. 1906, **39**, 638 ; D.R.P. 225232, 216772, 213500, 238488, 210019, 212436, 223510. Numerous recent additions to the acylaminoanthraquinone dyes described in the patent literature are not yet in common use. They are obtained for the most part by condensing one or more molecules of an aminoanthraquinone with complex acids such as quinoline-carboxylic acid, naphthalene-dicarboxylic acids, or perylenetetracarboxylic acids (B.P. 416425, 339267, 381090, 388889, 388096, 399790).

In this connection may be mentioned **Alizarin Indigo G**. This vat dye is obtained



by condensing dibromoisatin chloride with α-anthrol. The vat is yellowish-brown and it dyes cotton in pure greenish-blue shades of excellent fastness.

Figures giving the relative fastness of the anthraquinone dyes to light, washing, rubbing, ironing, sulphur, sweat, alkalis, acid-boiling, bleaching, potting, sea-water, fulling and steaming, and carbonisation with sulphuric acid are given in Schultz, " Farbstoff Tabellen," Leipzig, 1934. D. R.

ALIZARIN Astrol B, Bordeaux, Celestol R, Cyanine Green, Direct Blue A and B, Direct Green G, Direct Violet R, Geranol B, Irisol R, Rubinol R, Saphirol B, Sky Blue B, Uranols B and R, Viridine FF, *v.* ANTHRAQUINONE DYESTUFFS.

ALIZARIN GLYCOSIDES occur in the colouring matter of madder, the ground root of *Rubia tinctorum*. The best known of these is *ruberythric acid*, which is hydrolysed to glucose (2 mols.) and 1 : 2-dihydroxyanthraquinone (1 mol.). Others are *purpurin* and *rubiadin*, *q.v.* E. F. A.

ALIZARIN YELLOW. The numerous dyes of this name are not derivatives of alizarine, but are either azo dyes (*see* DYESTUFFS, Azo) or hydroxy-ketones.

ALKALI BLUE. *Nicholson's Blue.* A mixture of sodium triphenyl-*p*-rosaniline monosulphonate and sodium diphenyl-*p*-rosaniline monosulphonate.

ALKALI BORDEAUX, ALKALI BROWN, ALKALI DEEP BLACK, ALKALI FAST RED, ALKALI FAST YELLOW, ALKALI GARNET, ALKALI ORANGE, ALKALI RED are azo dyestuffs.

ALKALI FAST GREENS (By), ALKALI VIOLET are triphenylmethane dyestuffs (*q.v.*).

ALKALOIDS. The alkaloids are nitrogenous basic carbon compounds occurring mostly in plants, but a few animals, *e.g.* the salamander, contain bases similar in every respect to the typical vegetable alkaloids. The exact demarcation of the group is difficult ; generally the alkaloids may be said to contain heterocyclic nitrogen, to be soluble in solvents immiscible with water, and to have a complicated molecular structure. These characteristics are, as a rule, not possessed by the simpler amines and betaines derived from the amino-acids of proteins, nor by choline and other bases of general biological importance which, in contradistinction to the typical alkaloids, are not limited to one, or a few species of plants or animals. For a full account of these amines, betaines, choline, etc., *v.* Barger, " The Simpler Natural Bases," Longmans, 1914 ; M. Guggenheim, " Die biogenen Amine," Berlin, 1924. A list of books dealing with alkaloids is given at end of article.

The discovery of the first alkaloid is due to the German pharmacist Sertürner, who, in 1805, isolated from opium a substance " morphium," which he described more fully in 1817 as a basic, salt-forming substance having the principal physiological action of the drug. The discovery of morphine was quickly followed by that of other alkaloids made chiefly by Pelletier and Caventou. The first volatile alkaloid, coniine, was isolated in 1827 by Giesecke, and nicotine in 1828 by Posselt and Riemann.

Distribution and Mode of Formation.—No alkaloids have been obtained from algæ and mosses, hardly any from fungi, a few only from vascular cryptogams and gymnosperms, more from monocotyledons, but the vast majority from dicotyledons. Certain large orders, *e.g.* *Compositæ* and *Gramineæ*, are very poor in alkaloids, others such as the *Ranunculaceæ*, *Solanaceæ*, *Papaveraceæ* are typically rich. Generally an alkaloid is limited to a single genus or order ; berberine, however, occurs in several orders. The total alkaloids of a plant usually consist of a mixture of several bases often closely related, which may be present in very different amounts, *e.g.* aconitine, *q.v.*

The older view that alkaloids are plastic materials capable of further utilisation by plants has been disproved by Clautriau (Ann. Soc. belge de Microsc. 1894, 18 ; Ann. Soc. roy. Sci. méd. nat. Bruxelles, 1900, 9), who concludes that they are waste products, only of use as a means of defence on account of their poisonous properties. The amount of alkaloid is generally greatest in the mature plant and in the periphery (bark) or in hibernating parts (root) ; it varies greatly in different organs. Weight for weight young shoots and leaves may contain more than older ones. For methods of microscopical localisation, *see* Errera, Maistriau and Clautriau (Ann. Soc. belge de Microsc. 1888, 12 ; Clautriau, *ibid.* 1894, 18).

The mode of origin of alkaloids in plants is not understood and has given rise to much speculation (Czapek, Biochemie der Pflanzen, 1921, iii, 229 ; Windaus and Knoop, Beitr. chem. Physiol. Path. 1905, **6**, 392 ; Pictet, Arch. Sci. phys. nat. 1905, **243**, 329 ; 1906, **244**, 389 ; Tunmann, Arch. Pharm. 1910, **248**, 644 ; Winterstein und Trier, "Die Alkaloide," vol. I, 1927). The most fruitful contribution is probably that of Robinson (Trans. Chem. Soc. 1917, **111**, 876, and Fifth Pedler Lecture, J.C.S. 1936, 1079), who utilises only reactions which can be carried out in the laboratory at the ordinary temperature and shows how several of the principal alkaloids might be built up from ammonia, formaldehyde, ornithine, lysine and degradation products of carbohydrates, such as citric and acetonedicarboxylic acids. These substances are imagined to undergo aldol and similar condensations, and it is interesting to note that Robinson has actually synthesised tropinone in aqueous solution at room temperature from succindialdehyde, methylamine and calcium acetone-dicarboxylate (*see* Schöpf and Lehmann, Annalen, 1935, **518**, 1). Similar syntheses and transformations of quinoline and *iso*quinoline derivatives have been studied by Schöpf and his pupils (Annalen, 1932, **497**, 1, 7, 22 ; 1934, **513**, 190), by Späth and Berger (Ber. 1930, **63** [B], 2098), and by Hahn and Schales (Ber. 1935, **68** [B], 24).

The alkaloids may be classified chemically according to the heterocyclic rings in which nitrogen occurs, as derivatives of pyrrolidine (*e.g.* hygrine), of pyridine (*e.g.* arecoline), of piperidine (*e.g.* piperine), of glyoxaline (*e.g.* pilocarpine), of indole (*e.g.* physostigmine), of quinoline (*e.g.* quinine), and of *iso*quinoline (*e.g.* papaverine) ; another group contains alkaloids without heterocyclic ring, derivatives of aliphatic amines (*e.g.* narceine). Some alkaloids may be classified under two of the above or under additional groups ; thus atropine and cocaine contain both a pyrrolidine and a piperidine ring, caffeine contains a pyrimidine ring in addition to glyoxaline. No chemical classification can be complete, and a large number of alkaloids of insufficiently known constitution have perforce to be arranged according to the plants (or animals) from which they are derived.

Method of Extraction and Isolation.—Generally speaking, alkaloids, whether occurring in the free state or as salts of organic acids, are extracted from the finely powdered material by means of strong spirit. After distilling off the alcohol, the bases are extracted from the residue by dilute acids, liberated by the addition of ammonia or sodium carbonate and extracted by chloroform, ether or carbon tetrachloride. This gives the total alkaloidal content of the plant, except where a quaternary base is present, when methods similar to those employed for the simpler natural bases, *e.g.* precipitation with mercuric chloride or phosphotungstic acid, are utilised. Certain stable alkaloids may be extracted from a mixture of the finely powdered plant with lime or magnesia by an organic solvent ; in other cases (*e.g.* caffeine in tea) extractions with boiling water may be employed.

The "total alkaloids" of plants obtained by the above methods are mixtures for which no general method of separation can be given. In some cases caustic soda may be used to separate the phenolic from the non-phenolic bases ; in others, fractional extraction of the ether or chloroform solution of the bases with acid brings about a separation ; or, again, a fractionation may be effected by regenerating the bases from acid solution by an alkali in the presence of light petroleum or ether, in which only a part of the mixture is soluble. After suitable preliminary treatment on these lines, alkaloids often crystallise as the free base, but if not, it is generally possible to crystallise a salt with a strong or weak acid.

The choice of the proper acid is sometimes of great importance, *e.g.* for physostigmine the salicylate is the best salt, and for ergotoxine the phosphate. Acid oxalates are frequently valuable, whilst aurichlorides are useful for Solanaceous alkaloids and picrates for simple bases, but no general rule can be given. In exceptional cases it may be convenient to add an ethereal solution of the acid to that of the alkaloid in dry ether. Excess of acid should be avoided and the precipitated salt can be washed by decantation, filtered, and crystallised. For further information concerning the methods of separating and characterising alkaloids, *see* Allen's "Commercial Organic Analysis," vol. vii, 1927, 5–13, and the articles in this dictionary on CINCHONA, IPECACUANHA and OPIUM ALKALOIDS. For the large-scale manufacture of alkaloids consult J. Schwyzer, "Die Fabrikation der Alkaloide," Berlin, 1927, and Ullmann's "Enzyklopädie der technischen Chemie."

Physical and Chemical Characters of the Alkaloids.—Nearly all are solids, and these mostly crystalline ; a few (coniine, nicotine) are liquids and are volatile with steam. In a high vacuum even complex alkaloids, *e.g.* strychnine, may often be sublimed or distilled on a small scale. Most alkaloids are optically active ; the specific rotation of the free base in a dissociating solvent may differ considerably from that of the ion of a salt in the same solvent, and the two may have opposite signs (*e.g.* nicotine and its salts) (*cf.* Carr and Reynolds, Chem. Soc. Trans. 1910, **97**, 1328).

The majority of the typical alkaloids are insoluble or very sparingly soluble in water ; their best solvent is alcohol. Usually they are also dissolved by chloroform, less generally by ether, benzene or amyl alcohol, sometimes by light petroleum. Simple amines, betaines, purine derivatives, and quaternary alkaloids like columbamine, are often more soluble in water than in organic solvents. The aqueous solutions of the alkaloids are often strongly alkaline to litmus, but a few alkaloids which are acid amides (colchicine, caffeine, piperine) are so feebly basic that they may be extracted from acid solution by chloroform, owing to the extensive hydrolysis of their salts. In these cases the salts are mostly not obtainable in a pure crystalline condition. Alkaloidal salts are generally more or less readily soluble in water and in alcohol, but as a rule not in chloroform or ether. Salts of the more complex alkaloids may be very little soluble in excess of the acid, if the latter is highly dissociated (mineral acids or even oxalic acid).

The vast majority of alkaloids are tertiary bases. A few (carpaine, cytisine, ephedrine) are secondary, and the betaines, berberine, columbamine, etc., are quaternary bases. Primary bases are only found among amines derived from the amino-acids of protein and not among true alkaloids ; they seem to be formed only by bacteria and fungi.

Most of the alkaloids are monacid bases even when they contain several atoms of nitrogen in the molecule. Thus, pilocarpine with two, physostigmine with three, and ergotoxine with five nitrogen atoms are monacid bases. Quinine is the best known example of a *di*-acid alkaloid.

The majority of alkaloids contain oxygen in addition to carbon, hydrogen and nitrogen, but coniine, nicotine and sparteine are important exceptions. Oxygen is often present in the form of phenolic hydroxy, methoxy or methylenedioxy groups (*e.g.* alkaloids derived from quinoline and *iso*quinoline). Other forms of combination are alcoholic (*e.g.* codeine), ethereal (*e.g.* morphine), lactonic (*e.g.* narcotine), carboxy-alkyl (*e.g.* cocaine), ketonic (*e.g.* xanthaline), and as the acid amide group (*e.g.* caffeine).

General Alkaloidal Precipitants.—*Auric chloride*, $AuCl_3$, combines with alkaloidal hydrochlorides to form well-defined aurichlorides of the composition $B,HAuCl_4$, generally sparingly soluble in water, and obtained as pale yellow precipitates on mixing the gold and alkaloidal chlorides in aqueous solution. The aurichlorides may be recrystallised from alcohol or water acidulated with hydrochloric acid, and are most useful for characterising Solanaceous alkaloids. Occasionally gold chloride is reduced to metallic gold with formation of a red gold sol. The aurichlorides may be analysed by simple ignition, or by combustion, or by decomposition with hydrogen sulphide ; in the last case the alkaloid is recovered unchanged by making alkaline the filtrate from the gold sulphide and extracting with chloroform. In a few cases, when alcoholic solutions of gold chloride and of the alkaloid are mixed, stable crystalline salts (auric chloride compounds) of the composition $B,AuCl_3$ are obtained (Dunstan and Ince, Chem. Soc. Trans. 1891, **59**, 271). For other aurichloride compounds of abnormal composition, *see* Dunstan and collaborators (Chem. Soc. Trans. 1893, **63**, 201, 445 ; 1900, **77**, 57).

Platinic chloride in aqueous solution may precipitate platinichlorides of the composition B_2,H_2PtCl_6, which are generally more soluble than the aurichlorides and are analysed in the same way. In both cases the estimation of the chlorine may be useful. The chlorides of bases may be conveniently recovered from the aurichlorides or platinichlorides by shaking a solution of these with metallic " molecular " silver (Dudley, Biochem. J. 1929, **23**, 1064).

Picric acid precipitates the picrates from solutions of most alkaloidal salts, and these may often be crystallised (from water or alcohol). The alkaloid may be recovered by extracting it from alkaline solution by chloroform, or the picric acid may be removed from acid solution by shaking with ether or benzene. The picric acid is conveniently estimated without the loss of the alkaloid, by nitron (Busch, Ber. 1905, **38**, 861).

Picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) in alcoholic solution behaves similarly (*e.g.* Warren and Weiss, J. Biol. Chem. 1907, **3**, 327). The picrolonates are less soluble than the picrates, and are of most use when the base and its picrate are readily soluble in water (histidine, arginine).

The above four precipitants may be used for obtaining crystalline salts for analysis and characterisation. *Mercuric chloride* is occasionally used for the same purpose, but more frequently only for preparative purposes (*see* quaternary bases, above). The following reagents are more sensitive, but generally give only amorphous precipitates, unsuitable for analysis.

Bismuth potassium iodide (Dragendorff's or Kraut's reagent) has been used for isolating simple water-soluble bases, which are recovered by grinding up the brick-red precipitate with freshly prepared lead hydroxide. After filtration the last traces of lead are removed by hydrogen sulphide. Cadmium potassium iodide is also employed as a general alkaloidal precipitant.

Iodine dissolved in aqueous potassium iodide (Wagner's or Bouchardat's reagent) is one of the most general. In dilute solutions a reddish-brown precipitate is formed, which in strong solution aggregates at once to a greenish-black mass, and consists of periodides of variable composition. Many periodides crystallise from alcohol, the crystals being green by reflected and red by transmitted light (*cf.* herapathite, under QUININE). The recovery of the alkaloid from a periodide may be effected by decolorising with sodium thiosulphate or sulphur dioxide, and shaking out from alkaline solution or, if this is impossible, grinding up the periodide with " molecular " copper, when only the iodide of the base remains in aqueous solution.

Potassium mercuric iodide (Mayer's or Tanret's reagent), prepared by adding potassium iodide to mercuric chloride until the mercuric iodide at first precipitated is redissolved, is the best general reagent for detecting alkaloids, and may afford an extremely delicate test. Some alkaloids are most completely precipitated in neutral, others in faintly acid, a few in more strongly acid solution. In very dilute solution only an opalescence is produced, in more concentrated solution a yellowish-white flocculent precipitate occurs, from which the alkaloid may be recovered by suspension in water and passing hydrogen sulphide. In spite of its variable composition, the precipitate may be used to some extent for quantitative purposes (*see* next section).

Tannic acid is merely a colloidal precipitant for complex substances and precipitates alkaloids, along with some glucosides (glycosides), peptones, etc.

For a full discussion of the above and other alkaloidal reagents, *see* Allen's " Commercial Organic Analysis," 1927, vol. vii, 22–35.

Quantitative Estimation of Alkaloids. As a rule only the "total alkaloid" can be determined, although in a few cases of technical importance (*e.g.* cinchona and strychnos alkaloids, *q.v.*) individual alkaloids may be estimated in a mixture. The estimation of the total alkaloid is based on the same principles as the isolation. Keller (Schweiz. Wochenschr. f. Chem. u. Pharm. 1894, **32**, 44) mixes the finely powdered drug with magnesium oxide, or moistens it with ammonia and extracts it with ether or a mixture of ether and chloroform. An aliquot portion of the extract is shaken with dilute acid, the aqueous solution is rendered alkaline and again shaken several times with ether or chloroform. The alkaloid left on evaporation of the solvent may be weighed but in most cases it is more satisfactory to titrate it in aqueous or dilute alcoholic solution. Of the various indicators suggested methyl orange and methyl red are theoretically and practically the best in most cases; the latter indicator is said to be quite satisfactory for all the official alkaloids. In special cases hæmatoxylin is used and sometimes iodeosin (*see* Allen's "Commercial Organic Analysis," vol. vii, 1927, 17–20; and von Korczynski, "Die Methoden der exakten quantitativen Bestimmungen der Alkaloide," Berlin, 1913). The last-named compilation gives, *i.a.*, all the methods of the German Pharmacopœia; the U.S.P. may also be consulted. A different principle is involved in the use of Mayer's reagent which, as a rule, gives much less accurate results. As a titration method this is probably best employed in the form given it by Heikel (Chem.-Ztg. 1908, **32**, 1149, 1162, 1186, 1212). Potassium mercuric iodide is chiefly useful for quantities too small to be titrated with acid and should then be used in a nephelometric comparison with alkaloidal solutions of known strength (*cf.* Ramsden and Lipkin, Ann. trop. Med. Parasitol. 1918, **11**, 443, who thus estimate quinine in blood and urine with considerable accuracy; minute quantities of other alkaloids can doubtless be estimated in the same way). Minute quantities, *e.g.* of nicotine in insecticides, may also be estimated by precipitation with silico-tungstic acid, $SiO_2,12WO_3,26H_2O$, and ignition at 1,000°.

Toxicological Detection of Alkaloids.—The principles are similar to those involved in extracting alkaloids from plants but, owing to the minuteness of quantities present and the possible presence of putrefactive and other bases, great care is required. For details of the methods of Stas-Otto, Dragendorff, etc., *see* Wynter Blyth, "Poisons, their Effects and Detection," 1909; Kippenberger, Z. anal. Chem. 1895, **34**, 294; Schmidt, Pharm. Chem. ii, 1911, 1550–58. Colour reactions are of little use for identifying an unknown alkaloid, especially if impure (*v.* Allen's "Commercial Organic Analysis," 1927, vol. vii, 14). Pharmacological tests are much more useful.

Bibliography of Alkaloids.—The best up-to-date account of the subject as a whole is by T. A. Henry, "The Plant Alkaloids," London, 1924. A comprehensive account is also given by E. Winterstein and G. Trier, "Die Alkaloide," vol. I, 1927; vol. II, 1930; this work deals also with the formation and physiological action of alkaloids and includes the simpler bases. Less complete, although still mentioning many little-known alkaloids, but dealing mainly with the official ones, is E. Schmidt, Pharmazeutische Chemie, 1911, ii, 1541–1855. The analytical determination, technology and toxicology of the better known alkaloids is fully treated in Allen's "Commercial Organic Analysis," 1927, vol. vii. Standards and methods of estimation for alkaloids of medicinal importance are now to be found in the various national pharmacopœias (B.P. Appendix XIII, p. 594, and special articles; U.S.P., pp. 452–454, and special articles). G. B. and F. L. P.

ALKALOIDS, CLASSIFICATION OF. The alkaloids will be treated under their title or under one of the following groups, in which case the individual members will be cross-referenced to that group:

- ACONITE ALKALOIDS.
- CACTUS.
- CALABAR BEAN.
- CINCHONA.
- COCA.
- CONIUM.
- DELPHINIUM.
- ERGOT.
- HARMALA.
- HOLARRHENA.
- IPECACUANHA.
- ISOQUINOLINE ALKALOIDS.
- JABORANDI.
- LOBELIA.
- LUPIN.
- MITRAGYNE.
- OPIUM.
- POMEGRANATE ROOT BARK.
- QUEBRACHO.
- SENECIO.
- SOLANACEOUS.
- SOLANINES.
- SOPHORA.
- STRYCHNOS.
- TOBACCO.
- VERATRUM.
- YOHIMBOA.

G. B.

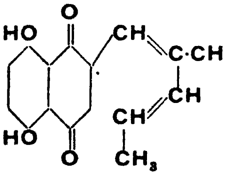
ALKANET. The Arabic name *Al-hennye*, modified to *alkanna* or *al-kenna*, was originally applied to the lythraceous shrub *Lawsonia alba* (Lam.), the root of which was described as *Radix Alkannæ vera*, in contradistinction to the root of our alkanna, which is *Anchusa tinctoria* (Lam.), and which became known as *Radix Alkannæ spuria tinctoria*. The latter, or *False Alkanet*, is also known as *Orcanette*, Fr.; *Orkanet*, Ger.; Languedoc bugloss or dyers' bugloss, *Radix Alkannæ spuria*. A plant with rough stalks, downy spear-shaped leaves and clusters of purplish or reddish flowers; belongs to the *Boraginaceæ*. Found in Asia Minor, Greece, Hungary, etc. The roots, which have an astringent taste, occur in commerce varying from the thickness of a quill to that of a finger.

Alkanet is one of the more ancient dyestuffs, having been employed by the Romans but, on the other hand, it does not appear at any time to have attained such importance as madder, indigo or even turmeric.

The colouring matter, *alkannin*, is present in the root to the extent of 5 to 6% (Jolin, Chem. Schriften über Alkanna, iv, 84 ; Thompson, Pharm. J. 1885–6, [iii], 16, 860 ; Eriksson, Ber. Deut. pharm. Ges. 1910, 20, 202). It is readily soluble in most of the usual solvents and its alkaline solution is coloured a deep-blue.

Alkannin has been the subject of extensive investigation and its composition, according to the earlier workers, was variously given as $C_{17}H_{10}O_4$ (Pelletier, Annalen, 1833, 6, 27), $C_{35}H_{20}O_8$ (Bolley and Wydlers, Annalen, 1847, 62, 141), $C_{15}H_{14}O_4$ (Carnelutti and Nasini, Ber. 1880, 13, 1514), and $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$ (Liebermann and Römer, Ber. 1887, 20, 2428). By distilling alkannin with zinc dust Liebermann and Römer obtained both methylanthracene and anthracene ; this suggested that alkannin was possibly an anthraquinone derivative.

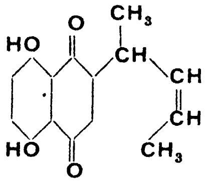
According to Raudnitz, Redlich and Fiedler (Ber. 1931, 64 [B], 1835), the spectroscopic behaviour of alkannin differs so widely from that of quinizarin and 5 : 6 : 7 : 8-tetrahydroquinizarin that its conception as an anthraquinone derivative cannot be maintained. By careful purification of the technical product, alkannin was obtained free from a previously undetected nitrogenous impurity and, after final purification through acetyl-leucoalkannin, was shown to possess the composition $C_{16}H_{14}O_4$. Catalytic hydrogenation of acetyl-leucoalkannin indicated the presence of two ethylenic linkings. When sublimed *in vacuo* at 300°, alkannin yields naphthazarin and when oxidised with dilute nitric acid it gives, like naphthazarin, oxalic acid. On these grounds and, taking into account the fact that Liebermann and Römer obtained anthracene and β-methylanthracene by the zinc dust distillation of alkannin, Raudnitz, Redlich and Fiedler conclude that alkannin is 5 : 8-dihydroxy-2-β-methyl-$\Delta^{\alpha\gamma}$-pentadienyl-1 : 4-naphthaquinone :



Dieterle, Salomon, and Nosseck (Ber. 1931, 64 [B], 2086) succeeded in isolating alkannin as micro-crystalline leaves, m.p. 120°. The composition assigned, $C_{15}H_{14}O_4$, was supported by the analysis of the *diacetyl* derivative,

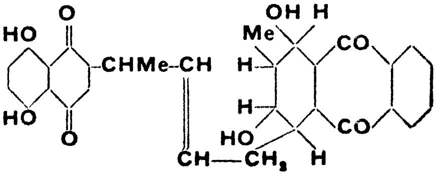
$$C_{15}H_{12}O_4Ac_2,$$

m.p. 147°, and of *tetra-acetyldihydroalkannin*, $C_{15}H_{12}O_4Ac_4$, m.p. 120°. These authors agree with Raudnitz, Redlich and Fiedler (*l.c.*) on the following points : two of the oxygen atoms are present as hydroxyl and two as carbonyl groups, while the relative positions of the groups in the above formula were confirmed by Dimroth's method (Ber. 1921, 54 [B], 3020). By the distillation of alkannin with zinc dust 2-methylanthracene was obtained. Ozonisation of alkannin yielded a *compound* $C_{13}H_8O_8$, m.p. 138°–139°, from which a *diacetyl* derivative, m.p. above 360°, was prepared. The compound, regarded as a dihydroxynaphthaquinone dicarboxylic acid, loses carbon dioxide when heated above its melting-point. Further ozonisation led to the formation of an *aldehyde*, $C_{11}H_6O_5$, characterised by a *phenylhydrazone*, m.p. 168°–169°, whilst subsequent ozonisation afforded oxalic acid. Experiment showed that the behaviour of alkannin differs from that of 1- or 2-methyl-1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxyanthraquinone. Further, the sublimation of 1-methyl-1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxyanthraquinone yields a *substance* $C_{13}H_8O_3$, m.p. 240°, whereas alkannin, on sublimation in high vacuo at 110°, gives 1-*methyl*-5 : 8-*dihydroxyanthraquinone*, m.p. 237°, and a *substance* $C_{12}H_{10}O_3$, m.p. 140°. By treatment of alkannin in acetic acid with hydrogen in the presence of palladium as catalyst, a *tetrahydro*-derivative is obtained. This loses two atoms of hydrogen by atmospheric oxidation yielding *dihydroalkannin*, m.p. 130°. Accordingly, Dieterle, Salomon and Nosseck assign the following constitution which differs slightly from that given above :



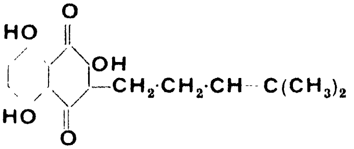
Raudnitz (Ber. 1932, 65 [B], 159) confirms the composition, $C_{16}H_{14}O_4$, he previously assigned to alkannin by re-analysis of tetra-acetyldihydroalkannin. The absorption spectrum indicated that the sublimation product derived from alkannin in high vacuo is naphthazarin and not 1-methyl-5 : 8-dihydroxyanthraquinone. Raudnitz considers it improbable that, under the conditions employed, Dieterle, Salomon and Nosseck (*l.c.*) actually prepared 1- or 2-methyl-1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxyanthraquinone, and if so their conclusions are erroneous.

Alkannin was isolated by Betrabet and Chakravarti (J. Indian Inst. Sci. 1933, 16 [A], 41) as a dark red powder which by digestion with sodium acetate and acetic anhydride at 140° for 5 hours gave a *tetra-acetyl* compound, brown crystals, decomposing at high temperatures. From this, by hydrolysis with methyl alcoholic potassium hydroxide and acidification, alkannin was obtained as a violet-red crystalline powder, decomposing at 220°, and having the composition $C_{30}H_{26}O_8$. A description of a number of derivatives is given. These authors conclude that alkannin contains two alcoholic and two phenolic hydroxyl groups and probably has the structure :



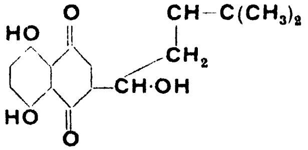
which explains why its absorption spectrum differs so widely from that of either naphthazarin or the hydroxyanthraquinones.

The difficulty in obtaining alkannin in a pure form is overcome, according to Raudnitz and Stein (Ber. 1934, **67** [B], 1955), by preparing the nickel salt, purifying this by extraction with water, alcohol and benzene, and cautiously decomposing it with 1% hydrochloric acid in methyl alcohol. The product crystallises from ether-alcohol in bronze-coloured needles (from concentrated solution) or dark-red gleaming spears (from dilute solution). The crystals, $C_{17}H_{18}O_5$, melt at 109° and contain one methoxyl group. Alkannin absorbs seven molecules of hydrogen by catalytic hydrogenation and by degradation with ozone yields 0·7 mol. acetone. *Tetra-acetyldihydroalkannin* melts at 133°–134°. These facts, in conjunction with earlier observations, indicate that alkannin is 5 : 8-dihydroxy-3(?)-methoxy-2-δ-methyl-Δ^{γ}-pentenyl-1 : 4-naphthaquinone, the position of the methoxyl group only being uncertain. Comment is made upon the fact that the 3-methoxyl compound would differ from shikonin :



(*Lithospermum erythrorhizon*, *q.v.*) only in that the 3-hydroxyl group is methylated, but whereas shikonin is partly converted by heating into 1 : 4-dihydroxy-8-methylanthraquinone, such a ring formation has never been observed with alkannin.

Brockmann and Roth (Naturwiss, 1935, **23**, 246) observe that alkannin, $C_{16}H_{16}O_5$, m.p. 149°, has the same composition, the same absorption spectrum, and almost the same melting-point as shikonin (m.p. 147°). An examination showed that they were not identical ; alkannin is lævorotatory whilst shikonin is dextrorotatory and is the optical enantiomorph of alkannin. Both substances by treatment with methyl-alcoholic hydrochloric acid yield the same optically inactive methoxyl derivative, m.p. 105° (*cf.* Raudnitz and Stein, *l.c.*). On the basis of numerous degradation experiments these authors assign the following formula to alkannin and shikonin :



Dyeing Properties.—As alkannin is insoluble in water, in dyeing with alkanet an alcoholic extract is usually employed ; and with aluminium and iron mordanted fabrics, violet and grey shades are respectively produced. These colours, however, are not fast to light and are somewhat readily affected by weak alkalis or acids.

Alkanet is now little if at all employed in Europe for ordinary dyeing purposes, but it is still used for colouring artificial wines, pomades, hair-oils, sweets, etc., and for these purposes it is well adapted on account of its ready solubility and harmless nature.

Böttger (Jahres. 1869, 843) and Enz. (*ibid.* 1870, 935) recommend the use of papers stained by alkanet as indicators in alkalimetry.

A. G. P. and E. J. C.

ALKANNA, AL-KENNA, or ALKANNIN *v.* Alkanet.

ALKASAL. *Alkasol.* Trade name for aluminium potassium salicylate,

$$Al_2[C_6H_3(OK)CO_2]_6.$$

Astringent and antiseptic.

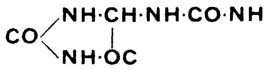
ALKASIL. Trade name for sodium silicate, Na_2SiO_3.

ALKYD RESINS. Glyptal resins. Trade name for condensation products of glycerol and phthalic anhydride used in varnishes (*cf.* Annual Report S.C.I. 1932, **17**, 360).

ALLANITE (*v.* Orthite). This is variously regarded as a synonym or as a variety of orthite. The original allanite was discovered at Kakarsuatsiak in east Greenland by C. L. Giesecke in 1806, described by T. Allen in 1808, and named by T. Thomson in 1810. Similar material has been found at numerous other localities in Greenland (O. B. Bøggild, Mineralogia Groenlandica, Meddel. om Grønland, 1905, **32**).

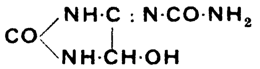
L. J. S.

ALLANTOIN. *Glyoxyldiureide*, $C_4H_6O_3N_4$

I. 

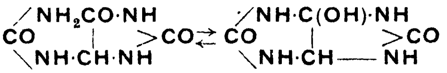
$$CO\begin{cases}NH\cdot CH\cdot NH\cdot CO\cdot NH_2\\ \quad\;\; | \\ NH\cdot OC\end{cases}$$

or

II. 

$$CO\begin{cases}NH\cdot C : N\cdot CO\cdot NH_2\\ \quad\;\; | \\ NH\cdot CH\cdot OH\end{cases}$$

or

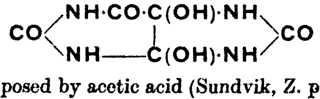


$$CO\begin{cases}NH_2CO\cdot NH\\ \qquad | \\ NH\cdot CH\cdot NH\end{cases}\!\!>CO \rightleftarrows CO\begin{cases}NH\cdot C(OH)\cdot NH\\ \qquad | \\ NH\cdot CH\text{——}NH\end{cases}\!\!>CO$$

(Titherley, J.C.S. 1913, **103**, 1336 ; Biltz, Ber. 1913, **46**, 3410 ; Mendel and Dakin, J.C.S. 1915, **107**, 434), was found originally in the allantoic liquid of cows by Vauquelin and Buniva (Lassaigne, Ann. Chim. Phys. 1821 [2], **17**, 301) and in the urine of newly-born calves (Wöhler, Annalen, 1849, **70**, 229) ; it occurs in the blood of the pig and ox (Hunter, J. Biol. Chem. 1917, **28**, 369) ; in beetroot (Smokenski, Z. Ver. deut. Zucker-Ind. 1910, 1251) ; in roots of *Phaseolus multiflorus* (Power and Salway, Pharm. J. 1913, [4], **36**, 552) ; in *Anabasis aretioides* and other plants (Stieger, Z. physiol. Chem. 1913, **86**, 269 ; Johnson, J. Amer. Chem. Soc. 1914, **36**, 1, 339) ; also in the young leaves, buds and stem of the plane tree (*Platanus orientalis*) ; sycamore (*Acer pseudoplatanus*) ; in the bark of the horse-chestnut (*Æsculus hippocastanum*) ; in comfrey root (Titherley and Coppin, Pharm. J. 1912, **34**, 92) ; and in rice polishings (Funk, J. Physiol. 1912, **45**, 75). Under normal conditions of growth

0·25 grm. allantoin may be isolated from 440 grms. of fresh young leaves of the plane, but when the branches are cut in bud and the buds allowed to open in water, the amount of allantoin increases to 0·5 or 1% of the dried leaves (Schulze and Barbieri, Ber. 1881, **14**, 1602 ; J. pr. Chem. 1882 [2], **25**, 145 ; Schulze and Bosshead, Z. physiol. Chem. 1884, **9**, 420). It has been found in the nitrogenous constituents of wheat-germs (Richardson and Crampton, Ber. 1886, **19**, 1180) ; in tobacco seeds (Scurti and Perciabosco, Gazzetta, 1906, **36**, ii, 626) ; and in crude beet juice (von Lippmann, Ber. 1896, **29**, 2652). Allantoin is a normal constituent of the urine of mammals ; the amount varies in different species, being greatest in the dog and least in man (Frerichs, Städeler, Jahresber. 1854, **7**, 714 ; Wiechowski, Biochem. Z. 1909, **19**, 368 ; Schittenhelm, Z. physiol. Chem. 1909, **63**, 248, 269, 283, 289). The whole quantity of allantoin excreted by man on a milk and vegetable diet may be derived directly from the food (Ackroyd, Biochem. J. 1911, **5**, 400). In the case of the dog the amount of allantoin in the urine is increased after a diet of animal food (Salkowski, Ber. 1878, **11**, 500), of calf's thymus (Cohn, Z. physiol. Chem. 1898, **25**, 507 ; Mendel, Amer. J. Physiol. 1902, **6**, xiv–xv ; M'Lachlan, Proc. Roy. Soc. Edin. 1906, **26**, 95) ; and on increasing the ingestion of water per day from 900 to 3,450 c.c. there is an increase of 20% in output (Fairhall and Hawk, J. Amer. Chem. Soc. 1912, **34**, 546). There is about 30% increase in elimination of allantoin if adrenaline is introduced (Falta, Z. exp. Path. Ther. 1914, **15**, 356). It is also increased after the administration of uric acid (Salkowski, Ber. 1876, **9**, 719 ; Swain, Amer. J. Physiol. 1910, **6**, 38 ; Wiechowski, Beitr. Chem. Physiol. Path. 1908, **11**, 109 ; Biochem. Z. 1910, **25**, 431), or of nucleic acid (Mendel, *l.c.* ; Schittenhelm, Z. physiol. Chem. 1910, **66**, 53 ; Wiechowski, *l.c.*). Allantoin is therefore to be regarded as an end-product of purine metabolism in the case of such animals as dogs and rabbits (Wiechowski, *l.c.* ; Schittenhelm, *l.c.* ; Hunter and Givens, J. Biol. Chem. 1914, **18**, 403).

The method of preparation of allantoin by oxidising uric acid with lead peroxide in presence of water is due to Liebig and Wöhler (Annalen, 1838, **26**, 245) ; it has been modified by Mulder (Annalen, 1871, **159**, 349), who effects the oxidation in dilute acetic acid solution and in bright daylight ; by this method 100 grms. of uric acid yield 30–32 grms. of allantoin. A quantitative yield of allantoin is obtained when uric acid is oxidised by an alkaline solution of potassium permanganate, and the intermediate compound



decomposed by acetic acid (Sundvik, Z. physiol. Chem. 1904, **41**, 343 ; Behrend, Annalen, 1904, **333**, 141 ; and 1915, **410**, 340). Allantoin is also obtained by the action of nitrous acid on dialuric acid (Gibbs, Annalen Suppl. 1870, **7**, 337). The synthesis of allantoin has been effected (1) by Grimaux (Compt. rend. 1876, **83**, 62) by heating a mixture of glyoxylic acid (1 part) and carbamide (2 parts) at 100° for 8–10 hours ; (2) by Michael (Amer. Chem. J. 1883, **5**, 198) by heating a mixture of mesoxalic acid and carbamide in equal proportions at 110° ; (3) by Simon and Chavanne (Compt. rend. 1906, **143**, 51) by the action of ammonia or alkali hydroxides on ethyl allantoate

$$CH(NH\cdot CO\cdot NH_2)_2CO_2Et$$

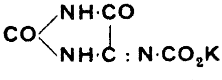
obtained by the condensation of ethyl glyoxylate with carbamide ; (4) by Behrend and Zieger (Annalen, 1915, **410**, 337) by condensing urea and alloxanic acid in boiling acetic anhydride ; (5) by Biltz and Giesler (Ber. 1913, **46**, 3424) by the action of potassium cyanate on 5-amino hydantoin hydrochloride ; and (6) by Biltz and Heyn (Annalen, 1916, **413**, 39) from *spiro*-5 : 5-dihydantoin by the action of barium hydroxide solution.

Allantoin is readily soluble in boiling water, sparingly so in cold (1 : 131·5 at 21·8°) (Grimaux, Ann. Chim. Phys. 1877 [v], **11**, 389) ; crystallises in glassy monoclinic prisms (Dauber, Annalen, 1849, **71**, 511 ; Hunter, J. Biol. Chem. 1916, **28**, 369) ; its heat of combustion at constant pressure is +413·8 kg.-cal. (*cf.* Emery, Benedict, Amer. J. Physiol. 1911, **28**, 303), and heat of formation +170·4 kg.-cal. (Matignon, Ann. Chim. Phys. 1893 [vi], **28**, 106). It melts at 227° (Titherley and Coppin), 235° (decomp.) (Watt, Pharm. J. 1917, **45**, 283), 235°–236° (decomp.) (Biltz and Heyn, *ibid.* 40) ; 232° (Hunter, *l.c.*).

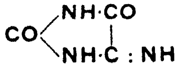
Allantoin was originally thought to be optically inactive (Mendel and Dakin, J. Biol. Chem. 1910, **7**, 153), but recently *l*-allantoin, $[\alpha]_D^{20°}$ 92·4° in water, has been obtained from inactive allantoin by the action of the allantoinases of soya bean and skate liver which preferentially hydrolyse the *d*-form. Formula I is thus upheld. The *d*-form $[\alpha]_D^{20}$+92° and the *dl*-form have also been isolated from the leaves of *Planatus orientale*. The active form racemises quickly in neutral or alkaline solution (Fosse, Thomas, and de Graeve, Compt. rend. 1934, **198**, 689, 1374, 1953).

Allantoin forms a silver salt $C_4H_5O_3N_4Ag$ (Liebig and Wöhler, *l.c.*) and a potassium salt $C_4H_5O_3N_4K$ (Mulder, *l.c.*) ; it also combines with certain metallic oxides to form sparingly soluble compounds ; the mercury, copper, zinc, lead, and cadmium derivatives are described by Limpricht (Annalen, 1853, **88**, 94).

Allantoin is oxidised by potassium ferricyanide in the presence of potassium hydroxide to potassium allantoxanate



(van Embden, Annalen, 1873, **167**, 39) ; the free acid does not exist, but breaks down, when liberated from its salts, into carbon dioxide and allantoxaidin



(Ponomareff, Ber. 1878, **11**, 2156). For oxidation of with bromine liquors (*see* Cordier, Monatsh. 1912, **33**, 759). Methylallantoin and isomerides (Fischer and Ach, Ber. 1899, **32**, 2745 ; Biltz and Heyn, Annalen, 1916, **413**, 83 and 97) ; 1-*methylallantoin* (α-methylallantoin), obtained from 9-methyl uric acid, has m.p. 250°–252° (decomp.), Fischer and Ach, m.p. 255°–259° (corr.) decomp. ; 3-methylallantoin (*β-methylallantoin*) crystallises in prisms with one molecule of water, m.p. 226°–227°, decomp., Fischer and Ach, m.p. 225°–227° (corr.) decomp. ; 3, 8-*dimethylallantoin* is obtained from 3, 7-dimethyl*spiro*-dihydantoin, m.p. 222°, turns yellow (decomp.) ; 1, 6-*dimethylallantoin*, obtained from 1, 9-dimethyl*spiro*-dihydantoin, m.p. 226°–227° (decomp.) (Biltz, Heyn and Bergius, Annalen, 1916, **413**, 77).

Several methods for the determination of allantoin, chiefly in urine, have been recorded. Plimmer and Skelton (Biochem. J. 1914, **8**, 70, 641) and y Costa (Bull. Soc. chim. biol. 1929, **11**, 965) estimate the ammonia formed after hydrolysis with hydrochloric acid. Christman (J. Biol. Chem. 1926, **70**, 173) converts allantoin to oxalic acid by hydrolysis with sodium hydroxide ; while Fosse, Brunel, Thomas and De Graeve (Compt. rend. 1929, **188**, 1418 ; 1931, **192**, 1615) convert it to allantoic acid with allantoinase from *Soya hispida*. Allen and Cerecedo convert allantoin to allantoic acid with potassium hydroxide (J. Biol. Chem. 1931, **93**, 293). For a rapid colorimetric method, *see* Larson (*ibid.* 1932, **94**, 727).

(For the method of estimating allantoin based on the sparing solubility of the silver and mercury derivatives, *see* Loewi, Z. anal. Chem. 1900, **39**, 266 ; Poduschka, *ibid.* 267).

Allantoin from even 0·1% solution can be precipitated nearly quantitatively with mercuric chloride and sodium hydroxide or carbonate (Hunter, J. Biol. Chem. 1916, **28**, 270).

M. A. W. and W. V. T.

ALLENES. The allenes are non-conjugated diolefinic hydrocarbons of the formula

$$RR'C : C : CR''R'''$$

(R, R′, etc.= H or alkyl) which are obtained (1) by the action of zinc dust and alcohol on dibromo- or dichloro-olefins of the type

$$CHR : CBr{\cdot}CHR'Br$$

(R, R′= H or alkyl), (2) by the action of zinc dust on tetrabromo- or tetrachloro-paraffins of the type $CHRCl{\cdot}CCl_2{\cdot}CHR'Cl$ (R, R′= H or alkyl), (3) by the action of potash or alcoholic potash at 130° on bromo-olefins and dibromo-paraffins of the types $CRR' : CBr{\cdot}R''$ and $CRR'Br{\cdot}CH : CR''R'''$ and $CRR'Br{\cdot}CHR''Br$ (R, R′ etc.= alkyl), (4) from ketones of the type $CHRR'{\cdot}CO{\cdot}CHR''R'''$ by the successive action of phosphorus pentachloride, and alcoholic potash at 130°, and (5) by isomerisation of certain alkylacetylenes on heating.

Allene, $CH_2 : C : CH_2$, the first member of the group, is prepared by the action of zinc dust and alcohol on dibromopropene :

$$CH_2 : CBr{\cdot}CH_2Br \xrightarrow{Zn} CH_2 : C : CH_2$$

It has also been obtained by electrolysis of potassium itaconate,

$$CH_2 : C(CO_2K){\cdot}CH_2{\cdot}CO_2K$$

(Aarland, J. pr. Chem. 1872 [ii], **6**, 266 ; 1873 [ii], **7**, 142), and by the action of heat on bromomethylacrylic acid, $BrCH : CMe{\cdot}CO_2H$ (Lossen, Annalen, 1905, **342**, 166).

Methylallene, $CHMe : C : CH_2$, b.p. 18°–19°, is prepared by passing ethyl alcohol together with acetaldehyde over very pure aluminium oxide at 360°–460° (Ostromisslenski, J. Russ. Phys. Chem. Soc. 1915, **47**, 1505), or by heating αββγ-tetrachlorobutane with zinc-copper couple in alcohol (Norton and Noyes, Amer. Chem. J. 1888, **10**, 430).

Ethylallene, $CHEt : C : CH_2$, b.p. 45°, has been obtained by the following series of reactions (Bouis, Ann. Chim. 1928 (x), **9**, 402) :

$$\begin{aligned} & CH_2 : CH{\cdot}CHO + MgEtBr \\ & \quad \rightarrow CHEt(OH){\cdot}CH : CH_2 \\ & \quad \xrightarrow{PBr_5} CHEt : CH{\cdot}CH_2Br \\ & \quad \xrightarrow{Br_2} CHEtBr{\cdot}CHBr{\cdot}CH_2Br \\ & \quad \xrightarrow{KOH} CHEtBr{\cdot}CBr : CH_2 \\ & \quad \xrightarrow{Zn} CHEt : C : CH_2 \end{aligned}$$

s.-*Dimethylallene*, $CHMe : C : CHMe$, b.p. 51°, is formed from βγγ-trichloro-pentan-δ-ol, $CHMeCl{\cdot}CCl_2{\cdot}CHMe{\cdot}OH$, by conversion of the alcohol into the corresponding chloride with phosphorus trichloride and dechlorination of the latter with zinc and alcohol (Favorski, J. pr. Chem. 1888 [ii], **37**, 392 ; Ipatieff, J. Russ. Phys. Chem. Soc. 1895, **27**, 362; J. pr. Chem. 1896 [ii], **53**, 272).

as.-*Dimethylallene*, $CMe_2 : C : CH_2$, b.p. 40°, is prepared by heating βγ-dibromo-β-methylbutane, $CMe_2Br{\cdot}CHMeBr$, or γ-bromo-β-methyl-Δ^{β}-butene, $CMe_2 : CBrMe$, with alcoholic potash (Favorski, J. pr. Chem. 1888 [ii], **37**, 392 ; Ipatieff, J. Russ. Phys. Chem. Soc. 1895, **27**, 362 ; J. pr. Chem. 1896 [ii], **53**, 272).

as.-*Diethylallene*, $CEt_2 : C : CH_2$, b.p. 97°, has been prepared by the action of alcoholic potash on the dichloride formed from diethylacetone by means of phosphorus pentachloride (Ipatieff, J. pr. Chem. 1899 [ii], **59**, 526) :

$$CHEt_2{\cdot}COMe \rightarrow CHEt_2{\cdot}CCl_2{\cdot}CH_3 \rightarrow CEt_2 : C : CH_2$$

and also by the action of potash at 130° on β-bromo-γ-ethyl-Δ^{β}-pentane, $CMeBr : CEt_2$, (Mereshkowski, J. Russ. Phys. Chem. Soc. 1913, **45**, 1971).

Properties.—The members of the group except allene itself, which is gaseous, are colourless liquids of garlic-like odour. The boiling-points of the higher allenes are given on page 241.

The allenes bear some resemblance in their superficial characteristics to the conjugated dienes but, unlike the latter, they display no exaltation of the molecular refraction and, in their additive reactions, no tendency towards the terminal addition of reagents such as bromine. Their molecules, unlike those of true acetylenes, contain no hydrogen atoms which can be directly replaced by metals. The allenes unite with hydrogen (2 mols.) in the presence of metallic catalysts somewhat less readily than do olefins and conjugated diolefins: the final products of reaction are the corresponding paraffins:

Alkyl-allenes	Formula	B.p. (°C.)
n-Propyl-	$CHPr:C:CH_2$	78
Trimethyl-	$CMe_2:C:CHMe$	72
as.-Methylethyl-	$CMeEt:C:CH_2$	70–71
n-Butyl-	$CHBu:C:CH_2$	106
as.-Diethyl-	$CEt_2:C:CH_2$	97
Tetramethyl-	$CMe_2:C:CMe_2$	86·5

$$CHMe:C:CH_2 \xrightarrow{2H_2} CH_2Me{\cdot}CH_2{\cdot}CH_3$$

With additive reagents of unsymmetrical constitution ($HClO$, HBr, etc.) all four of the possible ways of addition to the allene system appear to be exercised in greater or less degree, as may be symbolised thus (XY = addendum):

$$\begin{array}{lcl} >C:C:C< & \text{and} & C:C:C \\ X\cdots Y & & \quad X\cdots Y \\ Y\cdots X & & \quad Y\cdots X \end{array}$$

Additive attack appears in the main to begin at the central carbon atom of the allene system, giving in the case of unsymmetrical allenes chiefly products similar in type to those represented in the reactions (A) and (B) (Farmer and Sheikh, unpublished work):

$$\text{(A)}\ CHMe:C:CH_2+HOCl \rightarrow CHMe(OH){\cdot}CCl:CH_2$$

$$\text{(B)}\ CMe_2:C:CH_2+HBr \rightarrow CMe_2:CH{\cdot}CH_2Br$$

Doubtless the first stage of reaction results in the formation of such systems as

$$R_2\underset{|}{C}{\cdot}\underset{\cdot}{C}Cl:CH_2 \text{ and } R_2\underset{|}{C}{\cdot}CH:CH_2$$

$$(\text{or } R_2\underset{\oplus}{C}{\cdot}CCl:CH_2 \text{ and } R_2\underset{\oplus}{C}{\cdot}CH:CH_2),$$

which possessing the necessary structure for the occurrence of αγ-isomerisation would be potentially tautomeric:

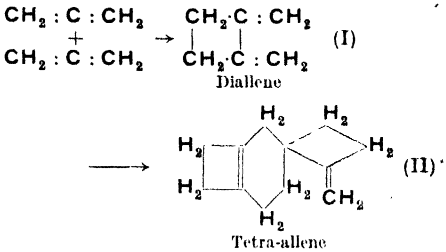
$$R_2\underset{|}{C}{\cdot}CCl:CH_2 \rightleftharpoons R_2C:CCl{\cdot}\underset{|}{C}H_2$$

$$R_2\underset{|}{C}{\cdot}CH:CH_2 \rightleftharpoons R_2C:CH{\cdot}\underset{|}{C}H_2$$

In these circumstances any real distinction between 2:1- and 2:3- addition disappears. The mono-addition products of allenes are mono-olefinic substances and behave as such.

Polymerisation.—Allene and its homologues undergo polymerisation on heating to give mainly volatile liquids, the molecules of which according to Lebedev (J. Russ. Phys. Chem. Soc. 1911, **43**, 820; 1913, **45**, 1249, 1357; J. Soc. Chem. Ind. 1913, **33**, 1224) are built up largely of *cyclo*butane rings. Allene is reported to give a dimeride of formula (I), which owing to its conjugated structure can itself undergo further polymerisation to give:

(i) a dimeride, *i.e.* tetrameric allene (II) of *cyclo*hexene type,



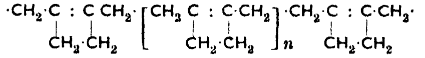
$$\begin{array}{l} CH_2:C:CH_2 \\ \qquad + \\ CH_2:C:CH_2 \end{array} \rightarrow \begin{array}{l} CH_2{\cdot}C:CH_2 \\ \ \,|\qquad | \\ CH_2{\cdot}C:CH_2 \end{array} \quad \text{(I)}$$

Diallene

(II)

Tetra-allene

(ii) higher polymerides of the general formula (III),

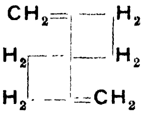


$$\cdot CH_2{\cdot}\underset{CH_2\cdot}{C}:\underset{CH_2}{C}CH_2{\cdot}\left[CH_2\underset{CH_2\cdot}{C}:\underset{CH_2}{C}{\cdot}CH_2\right]_n{\cdot}CH_2{\cdot}\underset{CH_2\cdot}{C}:\underset{CH_2}{C}{\cdot}CH_2\cdot$$

(III)

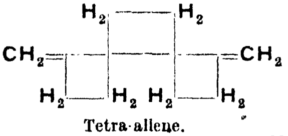
formed by the end-to-end linking of the conjugated diene system of the dimeride in the manner analogous to that which characterises high-polymeride formation from conjugated diene hydrocarbons, and

(iii) trimeric, tetrameric, and higher forms by the addition of molecules of monomeric allene successively to the dimeride, trimeride, etc., in the *cyclo*butane-forming manner, thereby yielding polycyclic structures such as (IV) and (V).



(IV)

Triallene.



(V)

Tetra-allene.

E. H. F.

ALLIONAL *v.* ALLONAL.

ALLOCHRYSINE. Trade name for sodium aurothiopropanolsulphonate,

$$AuSCH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3Na$$

Used for the treatment of tuberculosis.

ALLOCRYPTOPINE = β-Homochelidonine, *v.* ISOQUINOLINE ALKALOIDS.

ALLODELPHITE. Hydrous silico-arsenite of manganese,

$$5MnO{\cdot}2Mn_2O_3{\cdot}As_2O_3{\cdot}SiO_2{\cdot}5H_2O,$$

found as reddish-brown tabular crystals, probably orthorhombic, in manganese ore from Långban, Sweden. It shows a close relationship to synadelphite [$MnO{\cdot}(Mn,As)_2O_3{\cdot}2H_2O$] and is named from ἄλλος, other, and ἀδελφός, brother (P. Quensel and H. Eckermann, Geol. För. Förh. 1931, **52** (for 1930), 639).

L. J. S.

ALLOLACTOSE, $C_{12}H_{22}O_{11}$, is a disaccharide isolated from human milk serum along with *gynolactose* (Polonovski and Lespagnol, Compt. rend. 1931, **192**, 1319 ; 1932, **195**, 465).

It has reducing properties, is hydrolysed by emulsin to glucose and galactose, and may be identical with the synthetic glucose -6-β-galactoside (Helferich and Sparmberg, Ber. 1933, **66**, 806). E. F. A.

ALLONAL. *Allional.* Trade name for the dimethylaminophenyldimethylpyrazolone salt of allyl*iso*propylbarbituric acid, m.p. 93°. Sedative.

ALLOSAN. Trade name for santalyl allophanate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2{\cdot}C_{15}H_{23}$, m.p. 162°. Urinary antiseptic.

ALLOSE, $C_6H_{12}O_6$, m.p. 128°, $[\alpha]_D$ $-1{\cdot}9° \rightarrow -13{\cdot}9°$, is that stereoisomeride of glucose which has all the hydroxyl groups on the same side of the chain of carbon atoms.

l-Allose has been synthesised recently from *l*-ribose by the cyanhydrin reaction and is the last of the glucose sugars to be made. It is crystalline and exhibits mutarotation (Austin and Humoller, J. Amer. Chem. Soc. 1933, **55**, 2167 ; 1934, **56**, 1153).

d-Allose was made in the same way from *d*-ribose (Levene and Jacobs, Ber. 1910, **43**, 3141). E. F. A.

ALLOTROPY. It has been known for a long time that certain elements could exist in more than one solid form. The first known record is by Aristotle, who noted the change and break-up of ordinary tin when exposed to frost. This phenomenon was re-observed in Russia during the severe winter of 1867–68 when some blocks of tin stored in the Customs House at Petrograd crumbled to a grey powder. It has since been shown that this powder is the variety stable below 13°C. while above it ordinary tin is more stable. The two modifications are in equilibrium with one another at 13°C., which is known as the "transition temperature." Any element which can exist in two or more forms in the same phase is said to exhibit "allotropy" and the various forms of the element are known as "allotropes."

It is possible to represent the conditions of equilibrium for allotropes by means of TPx (pressure, temperature, composition) diagrams according to the principles of the Phase Rule. The element phosphorus is allotropic and the conditions for equilibrium between its phases are shown in Fig. 1, where the *x*-axis represents temperature in °C. and the *y*-axis the corresponding pressures. The area GBCH is the region in which crystals of ordinary white phosphorus are stable. C is the triple point of this material and CH represents the influence of pressure on its melting-point. At low temperatures and high pressures Bridgman (J. Amer. Chem. Soc. 1914, **36**, 1344) isolated a second form of white phosphorus which crystallises in the hexagonal system. The line BG shows the temperatures and pressures at which the above two modifications are in equilibrium and the point B where they can co-exist with vapour. AB, BC, and CD are the vapour pressure curves of hexagonal white, regular white, and liquid white phosphorus respectively. The two types of white phosphorus are said to be "enantiomorphic" as both have definite ranges of temperature and pressure over which they are stable, and, at a given pressure, there is a transition temperature where they are in equilibrium with one another.

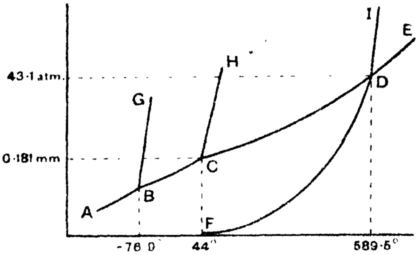


Fig. 1.

When yellow phosphorus is heated in a sealed tube it begins to change rapidly above 270°C. into a violet (so-called red) modification. This material cannot be reconverted into the yellow variety at any temperature or pressure. In other words, the yellow phosphorus is always metastable with respect to the violet and the former can only be obtained from the latter by taking it through the vapour phase, when the metastable modification tends to separate first. As there is no transition temperature violet phosphorus is said to be "monotropic" with respect to the white varieties. It is obvious that the above transformation will prevent the upper part of the vapour pressure curve CD being obtained experimentally, although by rapid working Smits and Bokhorst (Z. physikal. Chem. 1916, **91**, 349) were able to investigate a considerable portion of it and to show by extrapolation that it was a continuation of DE, the vapour pressure curve of liquid violet phosphorus. The remaining lines DI and DF represent respectively the influence of pressure on the melting-point and the sublimation pressures of violet phosphorus. The fact that these lines are always so much lower than the corresponding ones for white phosphorus emphasises the relative instability of the substance.

In the previous example no mention has been made of the molecular complexity of any given phase and it was tacitly assumed that only one molecular species was present. The same diagram would, however, be obtained if every phase consisted of a dynamic equilibrium of two or more molecular types. Many examples are known of systems of this type. Thus if a trace of sulphuric acid is added as a catalyst to acetaldehyde it will polymerise until a certain amount of paraldehyde is present :

$$3CH_3{\cdot}CHO \rightleftharpoons (C_2H_4O)_3$$

The relative amounts of aldehyde and paraldehyde present will vary with the temperature as shown by line ED in Fig. 2, and so, whatever the initial concentrations of the two materials were, they will finally freeze at the same temperature, 6·75°C. This is the "natural freezing-point" and corresponds with point D in the diagram. It should be noted that the stable solid, paraldehyde, separates from the equilibrium melt.

In the absence of the sulphuric acid as catalyst the transformation is slow and mixtures of acetaldehyde and paraldehyde behave as an ordinary binary system as shown by the lines AC and BC in Fig. 2. It is clear, therefore, that acetaldehyde-paraldehyde mixtures behave as a one- or as a two-component system depending on whether the time required for the establishment of equilibrium is small or large compared with the time required for the determination of the freezing-point or other physical property. On careful examination other materials, normally considered simple, can be shown to be mixtures, the properties of which vary according to the previous treatment of the sample. Thus the melting-point of white phosphorus is 44·1°C., but if the solid is heated very rapidly it begins to melt below 44·1° and if the liquid is rapidly cooled it begins to freeze above 44·1° ; the divergence varies with the rate of cooling and the initial temperature of the melt (Smits and Bokhorst, *l.c.*). A similar melting range has been observed by Smits with rhombic sulphur (Z. physikal. Chem. 1911, **76**, 421; 1913, **83**, 221). His results are shown in Fig. 3 where *bnn′*L and *bmm′*S represent the amounts of the *a* and *β* forms in the liquid and solid phases of the binary system. *k*L shows the proportions for inner equilibrium in the liquid and SS_1 in the solid state. The diagram shows that if inner equilibrium is first established at P′ (90°C.) and the melting-point rapidly determined, *m′* (110·9°C.) is reached before melting commences ; similarly from point P a still higher temperature is reached at *m* before the liquid can be formed. With normal working the natural melting-point of 110·6°C. is observed.

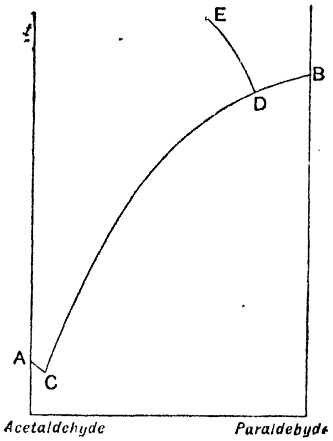


Fig. 2.

From these and similar observations A. Smits propounded a general theory of allotropy. He argued that the origin of allotropy in a phase was to be found in the complexity of that phase and therefore in the existence of "different molecular species." Thus any phase of an allotropic substance can under certain conditions behave as though it contained more than one component. When the system is unary these components are in inner equilibrium, but when equilibrium is not established it behaves like a system of higher order. By means of these assumptions it has been possible to represent all types of allotropic change and to bring forward explanations of phenomena like the passivity of iron and nickel in terms of their allotropy. It is, however, doubtful whether the applications of the general theory are as universal as was once supposed. The work of H. B. Baker (J.C.S. 1922, 568) and A. Smits and co-workers (J.C.S. 1926, 2657 ; 1928, 2399) indicated the existence of allotropic forms in materials normally considered simple, but subsequent experiments have so far failed to confirm these conclusions (H. V. A. Briscoe, J. B. Peel, and P. L. Robinson, J.C.S. 1929, 368 ; F. Daniells, Proc. Nat. Acad. Sci. 1928, **14**, 606 ; A. Smits and D. Cannegieter, Z. physikal. Chem. 1934, **171**, 445 ; 1935, **172**, 1). Similarly, the evidence in favour of the existence of apparent transition points in nitrobenzene, carbon disulphide, and ether (J. Mazur, Nature, 1930, **126**, 993 ; M. Wolfke and J. Mazur, Z. Physik, 1932, **74**, 110) has not been confirmed by later workers (A. Smits and H. Gerding, Z. physikal. Chem. 1932, **160**, 231).

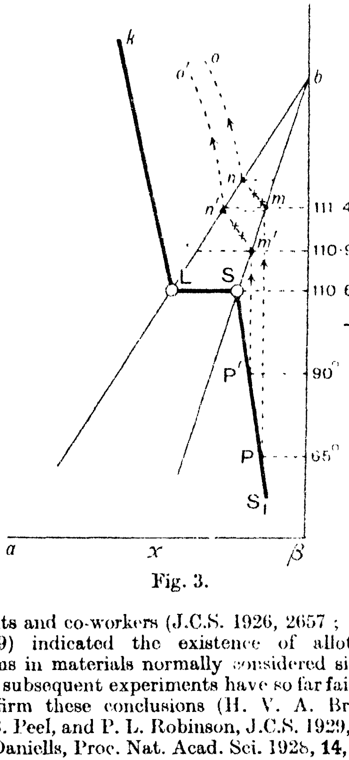
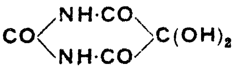


Fig. 3.

R. H. P.

ALLOXAN. *Mesoxalylcarbamide*, 2 : 4 : 5 : 6-tetraoxypyrimidine ; (1 : 3)-Pyrimidinetetrone,



$$CO\langle\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\rangle C(OH)_2$$

found by Liebig (Annalen, 1862, **121**, 81) and by Lang (Z. anal. Chem. 1867, **6**, 294) in certain pathological excretions, is one of the oxidation products of uric acid, and was first prepared by Brugnatelli (Ann. Chim. Phys. 1817, **8**, 201 ; from Giornale di Fisica, decade seconde, i, 117), under the name of *erythric acid*, by oxidising uric acid by means of nitric acid, chlorine or iodine. Liebig and Wöhler (Annalen, 1838, **26**, 256), who systematically studied the oxidation of uric acid, gave to this product the name of *alloxan*, regarding it as bearing the same relation to *allantoin* and *oxalic acid* that *oxaluric acid* does to *oxalic acid* and *urea*. According to Liebig and Wöhler (*l.c.*) and to Gregory (Mem. Chem. Soc. 1848, iii, 44), alloxan can be obtained most readily and with a yield of 90% by careful oxidation of uric acid by means of nitric acid, sp.gr. 1·412.

According to Schlieper (Annalen, 1845, **55**, 261), the oxidation of uric acid to alloxan is more conveniently effected with hydrochloric acid and potassium chlorate; 4 parts of uric acid are mixed with 8 parts of hydrochloric acid, and 1 part of finely powdered potassium chlorate added in successive small quantities, avoiding the liberation of chlorine; after two or three hours the dissolved alloxan is reduced by means of sulphuretted hydrogen to the sparingly soluble *alloxantin*. This is separated from admixed sulphur by crystallisation from hot water, and oxidised to alloxan by the action of diluted nitric acid. Biltz (Annalen, 1916, **413**, 60) prepares alloxan from uric acid in one operation by oxidation with chlorine.

Alloxan crystallises from warm saturated aqueous solution in large triclinic prisms containing $4H_2O$; it is also obtained in oblique rhombic prisms, belonging to the monoclinic system on evaporating an aqueous solution at 65°–70°. On exposure to the air or on heating at 100° it loses $3H_2O$, leaving the dihydroxy compound which has the composition expressed by the formula above (Lang, Grailich, J. 1858, 308; Hartley, J.C.S. 1905, **87**, 1802). The remaining molecule of water is lost at 150°. By heating under reduced pressure it is possible to dehydrate alloxan and also its mono- and dimethyl derivatives, all of which sublime unchanged in vacuum. The anhydrides form alcoholates from alcohols containing a little hydrochloric acid and these, when heated, eliminate a molecule of the alcohol and leave a residue with the melting-point of the anhydride (Biltz, Ber. 1912, **45**, 3659). *Alloxan anhydride* $C_4H_2O_4N_2$, yellow rhombic crystals, has m.p. 256° (decomp.).

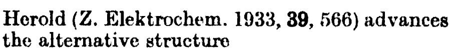
When crystals of alloxan are kept for some years in closed vessels they sometimes undergo spontaneous decomposition, forming alloxantin, parabanic acid, and carbon dioxide. According to Gregory (Annalen, 1853, **87**, 126), this is due to the presence of traces of nitric acid contained in the water of crystallisation. Similar phenomena were observed by Baumert (Pogg. Ann. 1860, **110**, 93), by Heintz (Pogg. Ann. 1860, **111**, 436), and by Otto (Annalen Suppl. 1865, **4**, 256). Cases of spontaneous explosive decomposition of alloxan are recorded by Wheeler and by Bogert (J. Amer. Chem. Soc. 1910, **32**, 809); the products of decomposition being carbon dioxide, carbamide, oxalic acid, and alloxantin (Gortner, J. Amer. Chem. Soc. 1911, **33**, 85).

The molecular heat of combustion of alloxan is 276·5 kg.-cal. (Matignon, Ann. Chim. Phys. 1893 [vi], **28**, 300); the dissociation constant is $2{\cdot}32\times10^{-7}$ (Wood, J.C.S. 1906, **89**, 1835). The dissociation constant K (in diazoacetic ester solution) $=0{\cdot}03542$, concentration of H ions $=0{\cdot}000920$, and the sp. conductivity at 25°, not deducting that of water, $1{\cdot}1\times10^{-6}=1{\cdot}27\times10^{-5}$ (Calcagni, Atti R. Accad. Lincei, 1916 [v], 25, i, 643). In common with the other simple ureides, alloxan shows no absorption bands in its spectrum (Hartley, J.C.S. 1905, **87**, 1815). The ultra-violet absorption spectrum has recently been studied by Heyroth and Loofbourow (J. Amer. Chem. Soc. 1934, **56**, 1728).

Alloxan is readily soluble in alcohol or water; the solution is acid to litmus, stains the skin purple, and imparts to it a curious and unpleasant odour. In its physiological action alloxan affects the central nervous system, producing first stimulation, then paralysis. When taken internally it is excreted in the urine as alloxantin and parabanic acid (Lusini, Chem. Zentr. 1895, ii, 311, 727, 838; Koehne, Chem. Zentr. 1894, ii, 296).

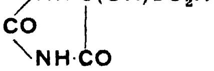
The equilibrium potentials of the system alloxan $\rightleftharpoons$ dialuric acid have been investigated by Richardson and Cannon (Biochem. J. 1929, **23**, 68). Luben and Getruener (Biochem. Z. 1933, **259**, 1) contrast the decomposition under influence of ultra-violet radiation with that of histidine, protamine, guanine, etc. Euler (Arkiv. Kemi, Min., Geol. 1927, **9**, No. 47, 1) has shown that alloxan is transformed by the action of *B. coli* into alloxanic acid, while this tendency to form alloxanic acid and also the ease with which alloxan is reduced by thiol groups (*e.g.* in cysteine) are suggested by Labes and Freisburger (Arch. exp. Path. Pharm. 1930, **156**, 226) to explain the toxicity of alloxan.

Alloxan is readily oxidised by warm dilute nitric acid, forming carbon dioxide and *parabanic acid* (*oxalylcarbamide*) (*q.v.*); is reduced by sulphuretted hydrogen, stannous chloride, zinc and hydrochloric acid, or by boiling with excess of sulphurous acid to *alloxantin* (*q.v.*); and is readily hydrolysed by alkali carbonates or by the hydroxides or chlorides of the alkaline earths, forming the corresponding salt of *alloxanic acid*. The barium and calcium salts are insoluble.



$$CO\begin{cases}NH\cdot CO\\NH\cdot CO\end{cases}CO+H_2O=CO\begin{cases}CO\cdot NH\cdot CO\cdot NH_2\\CO_2H\end{cases}$$

Herold (Z. Elektrochem. 1933, **39**, 566) advances the alternative structure



$$CO\begin{cases}NH\cdot C(OH)CO_2H\\NH\cdot CO\end{cases}$$

If, however, excess of alkali is employed or the solutions are heated, the hydrolysis is carried to completion with the formation of mesoxalic acid and carbamide (Schlieper, Annalen, 1845, **55**, 263; **56**, 1; Biltz, Annalen, 1916, **413**, 70). Alloxan gives a deep-blue colour with ferrous salts, but no precipitate is formed unless an alkali is present. According to Agrestini (Boll. Chim. farm. 1902, **41**, 5–7; Chem. Zentr. 1902, i, 631), the formation of blue colour is dependent on the presence of a trace of ammonia or caustic alkali, and the same deep-blue colour is also given by *pure* ferric salts under similar conditions. For similarity in the behaviour of triketohydrindene hydrate and alloxan, *see* Ruhemann (J.C.S. 1911, **99**, 793); Traube (Ber. 1911, **44**, 3145); Retinger (J. Amer. Chem. Soc. 1917, **39**, 1059). Alloxan gives the murexide reaction, and Agrestini (*l.c.*) finds that the ammonia in the reaction can be replaced by certain acid amides, amino-acids, or substituted amines; Rosenheim's alloxan test for choline (J. Physiol. 1905, **33**, 220), namely, the formation of a deep red-violet colour when a drop of a 1% solution of choline hydrochloride is evaporated on the water-bath with a few drops of a saturated solution of alloxan, is probably a reaction of the same order. These colour reactions with amino-acids and proteins are also described by Lieben and Edel (Biochem. Z. 1932, **35**, 2568).

Other tests for alloxan are (1) the formation of a deep violet-blue colour when a solution of alloxan is boiled for a few minutes with a drop of pyrrole, the colour changes to red on cooling, becoming green and then intensely blue on the addition of alkali. (2) The blue-green solution obtained on mixing concentrated sulphuric acid solutions of alloxan (or alloxantin) and pyrocatechol, the colour changes to an intense green on dilution (Agrestini, *l.c.*). Hartley (J.C.S. 1905, **87**, 1816) finds that hydrated alloxan, when powdered along with pure calcite, acquires a yellowish-pink tinge. After half an hour the colour is definite and it is permanent; on adding water a red solution is obtained. When alloxan, dried at 100°, is similarly treated, there is no colour developed until water has been added. Alloxanic acid gives no such colour reaction. Alloxan yields alcoholates, phenolates, and sulphites (Biltz, Ber. 1912, **45**, 3667–3670), also a compound with hydrogen peroxide $(C_4H_2O_4N_2)_{10}H_2O_2$ (Stolzenberg, Ber. 1916, **49**, 1545).

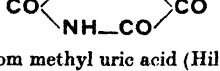
For the following derivatives of alloxan, *see* Behrend and Zieger (Annalen, 1915, **410**, 337):—

Potassium alloxan $C_4H_3O_5N_2K$, pale red needles, decomposes about 235°.

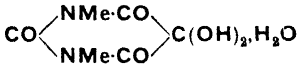
Urea alloxanate $C_4H_4O_5N_2,CO(NH_2)_2$, crystallises in four-sided prisms, decomposes at 155°–156°. Urea and alloxan tetrahydrate in cold aqueous solution form a crystalline substance, $C_5H_8O_6N_4$, which decomposes at 117° or 133°–134°, and is probably a salt-like compound of carbamide and alloxan monohydrate. It gives uric acid glycol when heated; boiled with acetic anhydride it yields an anhydride $C_5H_6O_5N_4$, microscopic needles, m.p. 185°–186°.

Methyl alloxanate $C_5H_6O_5N_2$, from alloxanyl chloride and methyl alcohol, prisms, decomposes 175°–176°.

The following homologues of alloxan have been described:—*Methylalloxan*

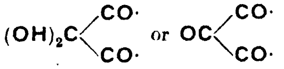


prepared from methyl uric acid (Hill, Ber. 1876, **9**, 1092); from ζ-uric acid (Fischer, Ber. 1899, **32**, 2731); from theobromine (Maly, Andreasch, Monatsh. 1882, **3**, 108; Fischer and Clemm, Ber. 1897, **30**, 3090). It crystallises from water in brilliant colourless prisms, becomes anhydrous at 60° in a vacuum, and decomposes at 156°. It is also prepared by oxidation of 1-methyl-5-benzylidene-barbituric acid with chromic acid in acetic acid solution (Biilmann and Berg, Ber. 1930, **63** [B], 2188; *cf.* Conrad and Reinbach, Ber. 1901, **34**, 1340). *Dimethylalloxan*

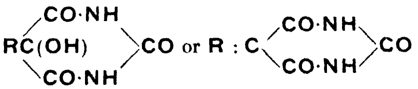


prepared by oxidising caffeine (Fischer, Annalen, 1882, **215**, 257; Maly, Andreasch, Monatsh. 1882, **3**, 96), by boiling dichlorodimethylbarbituric acid with water or silver oxide (Techow, Ber. 1894, **27**, 2083), loses $1H_2O$ when dried over sulphuric acid, decomposes at 100°; the anhydrous compound is a pale yellow powder soluble in alcohol and has m.p. 252°–255° (decomp.) (Biltz, Ber. 1912, **45**, 3659). *Diethylalloxan* $C_8H_{10}O_4N_2$, prepared by oxidising 1:3-diethylbarbituric acid with nitric acid, containing a little nitrous acid (Sembritzki, Ber. 1897, **30**, 1820). *Methylethylalloxan*, from ethyltheobromine by oxidation (Pommerehne, Apoth.-Ztg. 1897, **12**, 5); also in degradation products of 3:7-dimethyl-1-ethyluric acid (Biltz and Max, Annalen, 1917, **414**, 85). Some derivatives of *diphenylalloxan* have been described by Whiteley (J.C.S. 1907, **91**, 1344).

Inasmuch as the alloxan molecule contains the mesoxalyl radical



it forms a wide series of condensation products through the medium of the $:C(OH)_2$ or $:CO$ group yielding derivatives of the type



respectively. These compounds will be described under the following headings.

1. Condensation of Alloxan with Bisulphites.—Alloxan forms condensation products of the type $C_4H_2N_2O_4,NaHSO_3,1\frac{1}{2}H_2O$ with alkali bisulphites (Limpricht and Wuth, Annalen, 1858, **108**, 41), and with the sulphites of certain organic bases (Pellizzari, Annalen, 1888, **248**, 146). *Alloxan ethylamine sulphite* $C_2H_7N{\cdot}SO_3H_2{\cdot}C_4H_2N_2O_4,H_2O$; *alloxan aniline sulphite* $C_6H_7N{\cdot}SO_3H_2,C_4H_2N_2O_4,2H_2O$; *alloxan methylaniline sulphite*

$$C_7H_9N{\cdot}SO_3H_2,C_4H_2N_2O_4{\cdot}2H_2O;$$

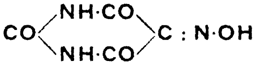
alloxan dimethylanilinesulphite

$$C_8H_{11}N{\cdot}SO_3H_2,C_4H_2N_2O_4,4H_2O$$

are described and the crystallographic constants are given. The *benzidine* compound contains $1H_2O$; *toluidine*, *aminobenzoic acid*, and *aspartic acid* yield similar compounds. *Alloxan pyridine sulphite* is triclinic, and anhydrous crystalline derivatives are afforded by *quinoline*, *picoline*, *morphine*, and *cinchonine*; the *strych-*

nine compound has $1H_2O$, and the *brucine* compound $1\frac{1}{2}H_2O$.

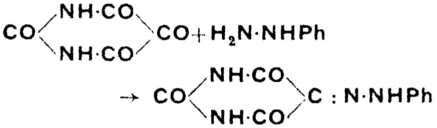
2. **Condensation of Alloxan with Hydroxylamine.**—Alloxan condenses with hydroxylamine hydrochloride (Ceresole, Ber. 1883, **16**, 1133) to form the 5-*oxime*, *violuric acid*



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}OH}$$

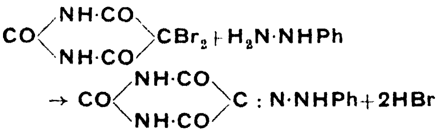
(*q.v.*). *Alloxan-6-oxime* (*iso*violuric acid), m.p. 250° (decomp.), is produced by treatment of *iso*barbituric acid with nitrous acid (Davidson, and Bogert, Proc. Nat. Acad. Sci. 1932, **18**, 490).

3. **Condensation of Alloxan with Hydrazines.**—Hydrazones of alloxan and its homologues can be prepared by the condensation of (*a*) the alloxan with the hydrazine :



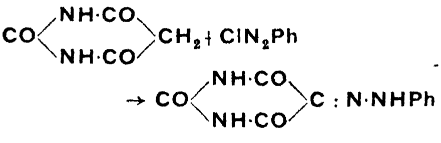
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{CO+H_2N{\cdot}NHPh}\rightarrow\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}NHPh}$$

(*b*) the dibromo-derivative of the corresponding barbituric acid with the hydrazine :



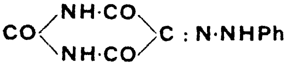
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{CBr_2+H_2N{\cdot}NHPh}\rightarrow\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}NHPh+2HBr}$$

(*c*) the corresponding barbituric acid with the diazonium chloride :



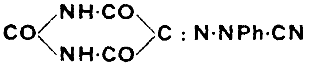
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{CH_2+ClN_2Ph}\rightarrow\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}NHPh}$$

And the following hydrazones have been prepared by one or more of these methods :—*Alloxan-5-phenylhydrazone*



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}NHPh}$$

pale-yellow crystals, melts and decomposes at 298°–300° ; *alloxan-6-phenylhydrazone*, m.p. 260°, from *iso*barbituric acid and benzene diazonium salts (Bogert and Davidson, Proc. Nat. Acad. Sci. 1932, **18**, 215) ; 1 : 3-*dimethylalloxanphenylhydrazone*, slender yellow crystals, m.p. 261°; the *o*- and p-nitro derivatives are yellow crystalline substances and decompose at 310° and 300° respectively (Kühling, Ber. 1891, **24**, 4140; 1898, **31**, 1972) ; *alloxanphenylmethylhydrazone*, brick-red hexagonal plates, decomposes at 189°–191° (Whiteley, Proc. Chem. Soc. 1906, **22**, 201) ; *alloxandiphenylhydrazone*, bright-yellow powder, melts above 270° (Armstrong and Robertson, J.C.S. 1905, **87**, 1291) ; 1 : 3-*diphenylalloxanphenylhydrazone*, bright-yellow needles that decompose at 265°, the p-*nitro* derivative forms yellow prisms with a purple reflex which melt and decompose at 274° ; 1 : 3-*diphenylalloxanphenylmethylhydrazone*, decomposes at 175° and crystallises in orange-red prisms or bright-yellow needles ; 1 : 3-*diphenylalloxandiphenylhydrazone*, melts and decomposes at 254°–255°, and forms yellow crystals yielding an orange-red powder on trituration ; 1 : 3-*diphenylalloxanphenylbenzylhydrazone*, melts and decomposes at 130°, crystallises from benzene in bright-yellow needles, and from methyl alcohol in bright-red prisms ; from toluene a mixture of the red prisms and yellow needles is obtained (Whiteley, J.C.S. 1907, **91**, 1344) ; *alloxancyanophenylhydrazone*

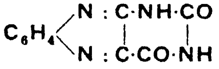


$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}\right\rangle\mathrm{C:N{\cdot}NPh{\cdot}CN}$$

from alloxan and aminophenylcyanamide, straw-yellow compound, m.p. 286° (Rolla, Gazzetta, 1907, **37**, i, 623) ; *alloxan-α-naphthylhydrazone*, m.p. 264°, from 5 : 5-dichloro- or dibromobarbituric acid and α-naphthylhydrazine (Nightingale and Schaeffer, J. Amer. Chem. Soc. 1932, **54**, 236 ; *see also* Guha and Dey, Quart. J. Indian Chem. Soc. 1925, **2**, 225 ; 1926, **3**, 41).

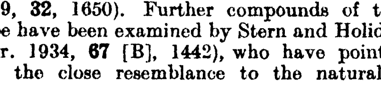
4. **Condensation of Alloxan with Semicarbazide.**—This reaction has been studied by Bromberg (Ber. 1897, **30**, 131). He describes the compounds *alloxansemicarbazide* $C_5H_9O_6N_5$ and *dimethylalloxansemicarbazide* $C_7H_{11}O_5N_5$, but was not successful in determining their constitution.

5. **Condensation of Alloxan with Diamines.**—In the condensation of alloxan with *o*-diamines the ketonic carbonyl and one of the adjacent carbimido-groups take part, and the product is an *azine* ; *alloxazine*



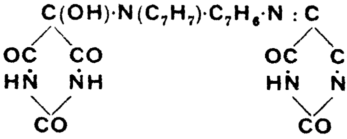
obtained from *o*-phenylenediamine, forms yellow microscopic crystals that decompose above 300° ; similar derivatives were obtained from 3 : 4-diaminotoluene and αβ-diaminonaphthalene (Kühling, Ber. 1891, **24**, 2363) ; for the effect of oxidising and reducing agents on these compounds, compare Kühling (Ber. 1895, **28**, 1968 ; 1899, **32**, 1650). Further compounds of this type have been examined by Stern and Holiday (Ber. 1934, **67** [B], 1442), who have pointed out the close resemblance to the naturally-occurring "photoflavins," while a red free radical has been prepared from alloxazine by Kuhn and Bär (Ber. 1934, **67** [B], 898).

The condensation of alloxan with monosubstituted *o*-diamines results in the formation of two compounds according as one or more alloxan molecules take part in the reaction. Thus alloxan condenses with *orthaminoditolylamine* at the ordinary temperature to form *alloxanylorthaminoditolylamine*



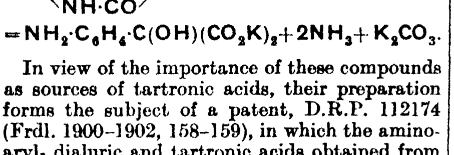
$$\mathrm{C_7H_7{\cdot}NH{\cdot}C_7H_6{\cdot}N:C}\left\langle\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}\right\rangle\mathrm{CO}$$

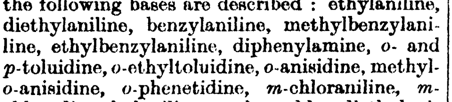
glittering yellow prisms, that melt and decompose at 252°, and dissolve in concentrated sulphuric acid with a deep red colour ; if, however, the condensation is effected in the presence of fuming hydrochloric acid and the mixture is boiled, *dialloxanylorthaminoditolylamine*



is formed. It is crystalline, and blackens at 300°, dissolves readily in alkali carbonates, and gives a deep-blue solution in concentrated sulphuric acid. Dimethylalloxan gives similar derivatives (Kühling, Ber. 1893, **26**, 540), and similar condensation products are obtained from alloxan and phenyl-*o*-phenylenediamine, *o*-aminodi-*p*-tolylamine, and *N*-methyl-*o*-phenylenediamine (Kühling and Kaselitz, Ber. 1906 ; **39**, 1314) ; and from tetramethyl-*m*-phenylenediamine (Sachs and Appenzeller, Ber. 1908, **41**, 91).

6. Condensation of Alloxan with Aromatic Amines.—Alloxan condenses readily with primary aromatic amines (Pellizzari, Gazzetta, 1887, **17**, 419) to form aminoaryl substituted dialuric acids (tartronyl carbamide), yielding on hydrolysis with alkali the corresponding tartronic acid (*q.v.*). Thus aniline and alloxan give *p*-amino-phenyldialuric acid, and this on hydrolysis yields *p*-aminophenyltartronic acid :





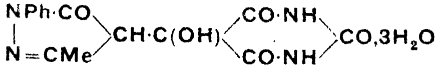
In view of the importance of these compounds as sources of tartronic acids, their preparation forms the subject of a patent, D.R.P. 112174 (Frdl. 1900–1902, 158–159), in which the aminoaryl- dialuric and tartronic acids obtained from the following bases are described : ethylaniline, diethylaniline, benzylaniline, methylbenzylaniline, ethylbenzylaniline, diphenylamine, *o*- and *p*-toluidine, *o*-ethyltoluidine, *o*-anisidine, methyl-*o*-anisidine, *o*-phenetidine, *m*-chloraniline, *m*-chlorodimethylaniline, and *m*-chlorodiethylaniline.

By careful oxidation with potassium permanganate of the alkali salts of the tartronic acids, or by oxidising the corresponding dialuric acid with mercuric oxide in presence of potassium hydroxide, the corresponding glyoxylic acid (*q.v.*) can be obtained :

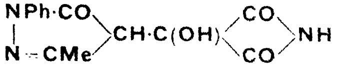
$$NH_2{\cdot}C_6H_4{\cdot}C(OH)(CO_2H)_2+O \\ =NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H+CO_2+H_2O$$

and the preparation by these methods of an important series of glyoxylic acids forms the subject of patents, D.R.P. 117021, 26/11, 1900 ; and 117168, 3/12, 1900.

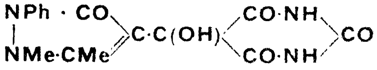
Alloxan condenses also with pyrazolone bases to form derivatives of dialuric acid, and these on hydrolysis with cold caustic alkali yield the corresponding substituted tartronimides (Pellizzari, Gazzetta, 1888, **18**, 340). Thus *phenylmethylpyrazolonetartronylcarbamide*



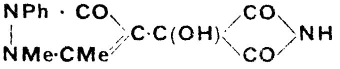
forms long yellow needles that decompose at 170°–178°, and yield *phenylmethylpyrazolonetartronimide*



on hydrolysis ; *phenyldimethylpyrazolonetartronylcarbamide*

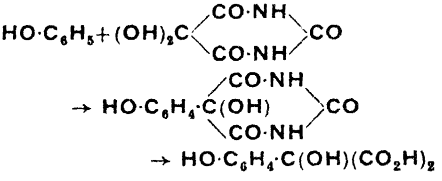


melts and decomposes at 261°, and yields *phenyldimethylpyrazolonetartronimide*



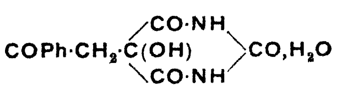
decomposing at 245°–250°.

7. Condensation of Alloxan with Phenols.—Alloxan condenses in the presence of hydrogen chloride, sulphuric acid or zinc chloride with mono- or polyhydroxy-phenols to form derivatives of dialuric acid that promise to be of value for pharmaceutical purposes, and are readily converted by hydrolysis into the corresponding tartronic acid :

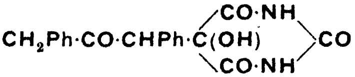


A description of the compounds obtained from alloxan and the phenolic compounds, phenol, *m*-cresol, *p*-cresol, guaiacol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, a-naphthol, is given in D.R.P. 107720, 25/8, 1898 ; 113722, 9/7, 1900 ; 114904, 17/9, 1900 ; and the tartronic acids derived from them are described in D.R.P. 115817, 8/10. 1900.

8. Condensation of Alloxan with Ketones.—Alloxan condenses with acetophenone and certain of its homologues to form phenacyldialuric acid or its derivatives, of which the following are described by Kühling (Ber. 1905, **38**, 3003) ; Kühling and Schneider (Ber. 1909, **42**, 1285) : *phenacyldialuric acid*

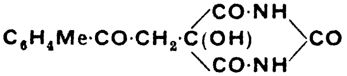


m.p. 212°, with decomposition ; the *bromo-derivative* decomposes at 217° ; *p-ethoxyphenacyldialuric acid* $C_{14}H_{14}O_6N_2$, m.p. 214° ; the *bromo*-derivative decomposes at 201° ; *αγ-diphenylacetonyldialuric acid*



$$CH_2Ph\cdot CO\cdot CHPh\cdot C(OH)\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}CO$$

m.p. 233° with decomposition ; p-*methylphenacyldialuric acid*



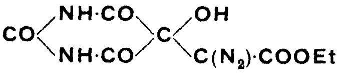
$$C_6H_4Me\cdot CO\cdot CH_2\cdot C(OH)\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}CO$$

m.p. 241°–242°, with decomposition ; the *acetyl* derivative decomposes at 220°, the *benzoyl* at 215° ; p-*methoxyphenacyldialuric acid*

$$C_{13}H_{12}O_6N_2$$

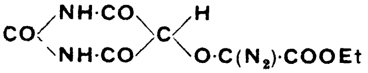
decomposes at 227°, and yields an *acetyl* derivative, m.p. 207°.

9. **Condensation of Alloxan into Ethyl Diazoacetate.**—Ethyldialuryl diazoacetate



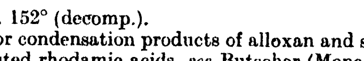
$$CO\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}C\begin{matrix}OH\\ C(N_2)\cdot COOEt\end{matrix}$$

or



$$CO\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}C\begin{matrix}H\\ O\cdot C(N_2)\cdot COOEt\end{matrix}$$

is prepared in 90–95% yield from alloxan hydrate and ethyl diazoacetate (Biltz and Kramer, Annalen, 1924, **436**, 154) ; it forms yellow plates and has m.p. 163°–164° (decomp.). The corresponding methyl ester forms yellow needles, m.p. 153°–154° (decomp.). Hydrolysis with dilute hydrochloric acid yields ethyl glycollate and alloxantin, whilst concentrated acid gives ethyl glyoxylate and dialuric acid, and in each case ethyl uracil carboxylate is also formed. Reduction with hydrogen iodide yields alloxantin and ethyl iodoacetate, and with stannous chloride, dialuric acid and glycollic acid; oxidation yields, according to the conditions, alloxan and oxalic acid or *dialurylglyoxylic acid*



$$CO\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}C\begin{matrix}OH\\ CO\cdot CO_2H\cdot 2H_2O\end{matrix}$$

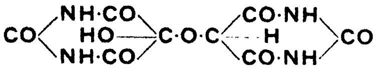
m.p. 152° (decomp.).

For condensation products of alloxan and substituted rhodamic acids, *see* Butscher (Monatsh. 1911, **32**, 9–19); and alloxan with aminoantipyrine, *see* Meyer (Compt. rend. 1911, **152**, 1677). M. A. W. and W. V. T.

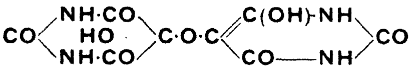
ALLOXANIC ACID *v.* Alloxan. *See also* Behrend and Zieger (Annalen, 1915, **410**, 337) ; Biltz, Heyn, Bergius (Annalen, 1916, **413**, 368) ; Biltz (Annalen, 1921, **423**, 301).

ALLOXANTIN, $C_8H_6O_8N_4,2H_2O$ (Ritthausen, Ber. 1896, **29**, 892), exists in small quantities in crude beet-juice (von Lippmann, Ber. 1896, **29**, 2645), and forms 34 to 36% of the products when *convicin* from sow-beans (*Vicia faba minor*) or from vetches (*Vicia sativa*) is hydrolysed by dilute mineral acids (Ritthausen, *l.c.* ; J. pr. Chem. 1899 [ii], **59**, 487). Johnson (J. Amer. Chem. Soc. 1914, **36**, 337–343) discusses its origin in plants. Alloxantin was prepared by Liebig and Wöhler (Annalen, 1838, **26**, 262) by oxidising uric acid with dilute nitric acid ; by the direct union of alloxan and dialuric acid ; and by reducing a cold aqueous solution of alloxan with sulphuretted hydrogen or stannous chloride. According to Vitali (Chem. Zentr. 1898, i, 665, from Boll. Chim. farm. **37**, 65), the reduction can also be effected by means of hydriodic acid. Alloxantin was synthesised by Grimaux (Compt. rend. 1878, **87**, 752) by heating malonic acid, carbamide and phosphoryl chloride at 150°, and passing sulphuretted hydrogen through a nitric acid solution of the crude product ; or by passing sulphuretted hydrogen through a hot aqueous solution of dibromobarbituric acid (Compt. rend. 1879, **88**, 86). Koech (Annalen, 1901, **315**, 246) describes the conversion of *iso*dialuric acid into alloxantin by heating it with guanidine and acetic acid ; the change seems to be due to the transformation of the *iso*dialuric acid into dialuric acid by the action of the base, and the subsequent oxidation of the dialuric acid to alloxantin, since, if the reaction is conducted in an atmosphere of carbon dioxide, dialuric acid only is obtained. An aqueous suspension of alloxantin possesses considerable oxygen-consuming power; it is probable that the ease of oxidation is due to dissociation in solution into alloxan and dialuric acid, the latter being auto-oxidisable (Thunberg, Skand. Arch. Physiol. 1916, **33**, 217).

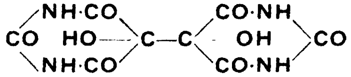
Alloxantin crystallises from aqueous solutions in small, sharp, rhombic prisms, containing $2H_2O$; it becomes anhydrous after heating for 1–1½ hours at 150°, or for 5 hours at 107°–110° ; it decomposes at 170° into hydurilic acid, ammonia, carbon monoxide, carbon dioxide, and oxalic acid ; turns yellow at 225°, and decomposes at 253°–255° (Biltz, Ber. 1912, **45**, 3675). It is decomposed into barbituric acid and parabanic acid when heated with concentrated sulphuric acid at 120°, and into allituric acid $C_6H_6O_4N_4$ when boiled with excess of hydrochloric acid (Schlieper, Annalen, 1845, **56**, 20). Alloxantin is sparingly soluble in cold water (0·2885 grm. per 100 c.c. at 25°, of which about 22% is undissociated—Biilmann and Bentzon, Ber. 1918, **51**, 522), yielding an acid solution that reduces solutions of silver salts, and gives a characteristic violet-blue precipitate with baryta water, changing on warming into the colourless barium alloxanate which undergoes further decomposition into barium mesoxalate and barium carbonate (Liebig and Wöhler, Annalen, 1838, **26**, 312). The barium salt has been isolated by Hantzsch (Ber. 1921, **54** [B], 1268) as a dark violet amorphous powder, $C_8H_2O_8N_4Ba_2$. Violet alkali metal salts have also been prepared. These salts regenerate alloxantin when acidified with moderately concentrated hydrochloric acid. Alloxantin has a molecular heat of combustion=584·7 kg.-cal. (Matignon, Ann. Chim. Phys. 1893 [vi], **28**, 323), and a freshly prepared aqueous solution shows a remarkable absorption band in the ultraviolet, which disappears upon keeping the solution owing to the decomposition of the alloxantin into alloxan and dialuric acid (Hartley, J.C.S. 1905, **87**, 1814). For this reason Hartley expresses the constitution of alloxantin by the formula



(*ibid.* 1819 ; *see also* Biilmann and Bentzon, Ber. 1918, **51**, 522 ; Slimmer and Stieglitz, Amer. Chem. J. 1904, **31**, 661) ; Piloty and Finckh (Annalen, 1904, **333**, 22) found that alloxantin was resolved into alloxan and dimethylamine dialurate, by boiling with dimethylamine acetate, and suggest the constitutional formula



in which the relationship between alloxantin and alloxan is the same as that existing between quinhydrone and quinone. In diazo-acetic ester the dissociation constant is 0·0006331, concentration of H ions 0·00001644, and sp. conductivity at 25° (not deducting that of water $1{\cdot}1\times10^{-6}$), $1{\cdot}13\times10^{-5}$ (Calcagni, Atti R. Accad. Lincei, 1916 [v], **25** i, 643 ; *see also* Richter, Ber. 1911, **44**, 2155 ; Johnson, J. Amer. Chem. Soc. 1914, **36**, 337). The conventional formula



is still used by Biltz (Ber. 1930, **63** [B], 2188) and Retinger (J. Amer. Chem. Soc. 1917, **39**, 1059) bases his theory of the colour of the salts on this formula.

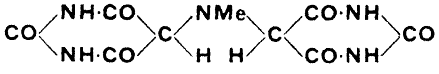
The spectra of these coloured salts have been examined by Gaind and Dutt (Bull. Acad. Sci. Agra and Oudh, 1933, **3**, 79).

Alloxantin is readily converted into murexide (*q.v.*) by the action of ammonia; into alloxan by mild oxidising agents; and into dialuric acid by reducing agents. In its physiological action alloxantin resembles alloxan, but is especially poisonous to cold-blooded animals, the blood showing strong reducing properties ; when taken internally it appears in the urine as parabanic acid, and in smaller quantities as dialuric acid, murexide, and alloxantin itself (Kowalewski, Chem. Zentr. 1887, 1296 ; Susini, Ann. Chim. farm. 1895, **21**, 241 ; 1896, **22**, 341, 385).

Acetylalloxantin $C_{10}H_8O_9N_4,H_2O$, obtained by the interaction of acetyl dialuric acid and alloxan, crystallises in thin leaflets, becomes anhydrous when kept in a vacuum over sulphuric acid, melts and decomposes at 263°–265°, and is slowly hydrolysed by hot water with the formation of alloxantin.

Benzoylalloxantin $C_{15}H_{10}O_9N_4,H_2O$, similarly formed from benzoyl dialuric acid and alloxan, crystallises in colourless six-sided plates, and melts at 253°–255° (Behrend and Friedrich, Annalen, 1906, **344**, 1).

Alloxantin is decomposed when boiled in an aqueous solution of the hydrochloride of a primary amine, yielding alloxan, together with the corresponding *dibarbiturylalkylamine*. These are colourless crystalline dibasic acids, hydrolysed by boiling with aqueous alkali hydroxides into dialuric acid and the amine. *Dibarbiturylmethylamine*

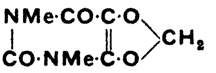


decomposes at 280°, *dibarbiturylethylamine* decomposes at 235°, *dibarbiturylphenylamine* becomes blue at 240°, *dibarbituryl-a-naphthylamine* becomes black at 260°, the corresponding *β*-compound decomposes at 260°, and *dibarbiturylcarbamide* $CO(NH{\cdot}C_4H_3O_3N_2)_2$ decomposes above 300°.

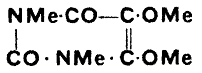
The following homologues of alloxantin have been prepared : *methylalloxantin* $C_9H_8O_8N_4$, $3H_2O$ from methylalloxan and dialuric acid (Andreasch, Monatsh. 1882, **3**, 431) ; sym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4,4H_2O$ from methylalloxan (Maly, Andreasch, Monatsh. 1882, **3**, 109), unsym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4$, H_2O from dimethyldialuric acid and alloxan (Andreasch, Monatsh. 1882, **3**, 428). *Tetramethylalloxantin* $C_{12}H_{14}O_8N_4$ *amalic acid* (from ἁμαλός = soft, so called on account of its feebly acid reaction), prepared (1) by oxidising caffeine with chlorine or nitric acid (Rochleder, Annalen, 1849, **71**, 1) ; (2) by reducing dimethylalloxan with sulphuretted hydrogen (Fischer, Ber. 1881, **14**, 1912) or with stannous chloride (Andreasch, Monatsh. 1895, **16**, 19) ; (3) from dimethyldialuric acid and dimethylalloxan (Maly and Andreasch, Monatsh. 1882, **3**, 105) ; (4) by the electrolysis of caffeine in sulphuric acid solution (Pommerehne, Arch. Pharm. 1897, **235**, 365). *See* Biltz (Ber. 1912, **45**, 3673) for the preparation of *dimethyl-* and *tetramethylalloxantin* from theobromine and caffeine respectively. In the preparation of dimethyl- and tetramethylalloxantins from these sources, Biltz (*l.c.*) suggests the use of cold stannous chloride and hydrochloric acid in preference to hydrogen sulphide. He defends this method of preparation (Ber. 1932, **65** [B], 565) against the criticism of Biilmann and Mygind (Bull. Soc. chim. 1930 [iv], **47**, 532).

Diethylalloxantin is obtained by oxidation of 6-ethyluric acid (Biilmann and Bjerrum, Ber. 1917, **50**, 837) or of 3 : 7 : 9-triethyluric acid with potassium chlorate and hydrochloric acid (Biltz and Sedlatscheck, Ber. 1924, **57** [B], 175). Various other homologues are described by Biilmann and Berg (Ber. 1930, **63** [B], 2188).

Tetraethylalloxantin $C_{16}H_{22}O_8N_4$, obtained by reducing diethylalloxan, melts and decomposes at 162° (Sembritzki, Ber. 1897, **30**, 1821). Alloxantin, with diazomethane, yields 5 : 6-methylenedioxy-1 : 3-dimethyluracil (I) and 5 : 6-dimethoxy-1 : 3-dimethyluracil (II), which are also formed when alloxan and dialuric acid are separately treated with diazomethane.

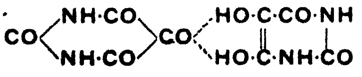


I.



II.

The co-ordination formula



has been proposed by Biltz and Paetzold (Annalen, 1923, **433**, 64) to account for the extraordinary ease with which alloxantin undergoes fission. An alternative explanation is advanced by Arndt, Eistert, and Ende (Ber. 1929, **62** [B], 44).

The hydrogenation potentials of alloxantin and its homologues have been investigated by Biilmann and Lund (Ann. chim. 1923 [ix], **19**, 137), Hill and Michaelis (Science, 1933, **78**, 485), and Biilmann and Mygind (*l.c.*). M. A. W.

ALLOXAZINE *v.* ALLOXAN.

ALLOYS. *See* individual metals, AMALGAMS, and METALLOGRAPHY.

ALLOYS, LIGHT. By the "light alloys" are meant those of aluminium and of magnesium. The specific gravity of the aluminium alloys generally ranges from 2·68 to 2·99, while that of the magnesium alloys is in the region of 1·82.

ALUMINIUM ALLOYS.

From the almost limitless number of possibilities in the way of chemical composition there has been developed a comparatively small number of important alloys which comprise the greater part of commercial production. These generally contain less than 15% of added elements. The choice of composition is determined not only by desired properties but also by considerations of fabrication and, in some cases, of cost. Alloys suited to casting are not in general suited to forging and it is convenient and usual in the metal industry to classify the alloys under the two heads. In general the casting alloys contain higher percentages of alloying constituents than the forging alloys, since higher additions facilitate casting but make working more difficult.

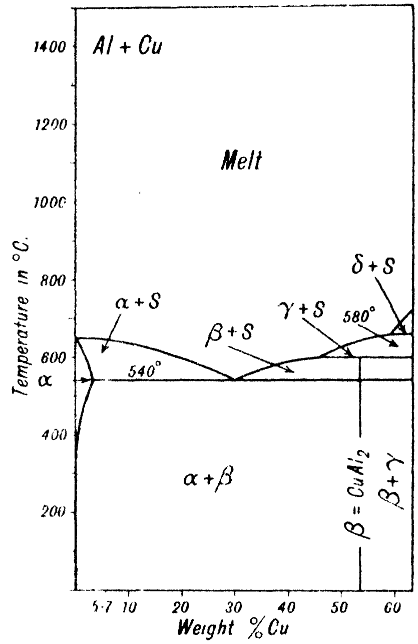
Casting Alloys.—Pure aluminium, as most other pure metals, is possessed of only a low tensile strength and it is soft and malleable.

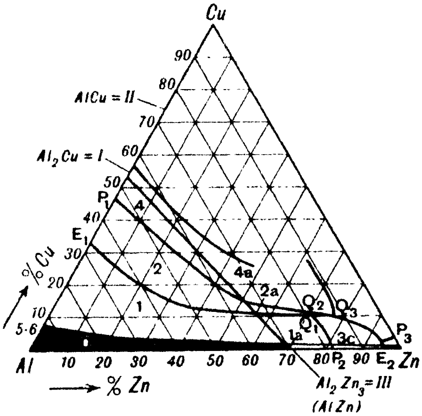
One of the first elements to be added to aluminium as a "hardener" was *zinc.* The alloys are easy to prepare by direct combination of aluminium and zinc, no intermediate alloy being necessary, and the straight binary alloys have good mechanical properties which do not deteriorate with mechanical working in the light alloy range (up to 15% zinc); they have also excellent machining properties. Their great disadvantage, however, is their tendency to lose strength at high temperatures. As a consequence of this fact the simple aluminium-zinc alloys are now rarely used.

Copper is the most important hardening element in aluminium light alloys and gives rise to some extremely valuable casting alloys, both alone and with zinc or other alloying constituents. The equilibrium diagrams of the aluminium-copper and aluminium-copper-zinc systems are produced below.

In the binary alloys (**Al-Cu**) the compound **CuAl$_2$**, containing approximately 54% **Cu**, forms a eutectiferous series with aluminium. The solubility of copper in solid aluminium decreases with decreasing temperature, being 5·5% at the eutectic temperature of 548°C.

The solid solution of copper in aluminium has been shown to have the face-centred cubic lattice characteristic of pure aluminium, so that solution of copper is apparently effected by simple substitution of copper atoms for aluminium atoms. In the useful alloys, containing generally less than 14% copper, solidification begins with the formation of dendritic crystals of aluminium containing a small





0.—Ternary solid solution (*a*).
1.—$a+Al_2Cu+(AlZn)$?
1*a* and 2.—$a+AlZn$.
2*a*.—$Al_2Cu+AlZn+CuZn+$ some *a*.
3.—Different constituents crystallise out along boundaries, and alloys in this field may contain several different eutectic mixtures.
4 and 4*a*.—$AlCu+Al_2Cu$.

amount of copper in solid solution : some segregation usually occurs even in alloys with as low a concentration as 2% copper.

The mechanical properties of a range of (chill) cast aluminium-copper alloys are shown below. The tensile strength increases as the copper content increases, up to a maximum of 8% copper : the elongation correspondingly decreases.

Cu %.	U.T.S. Tons per sq. in.	Elongation %.	Brinell Hardness.
3·5	10·2	18·0	54
6·0	11·5	10·0	60
9·0	12·4	6·0	72
12·0	12·6	2·3	89

The most commonly used alloy is that with about 8% copper. British Aircraft Specifications exist for this and for the alloy with 12% copper (**L11** and **L8** respectively) and similar compositions are widely used both in America and on the Continent. The aluminium-copper alloys are easily handled in all stages of manufacture. They may be prepared by the direct addition of copper to the molten aluminium, but it is generally considered preferable to use a 50 : 50 copper-aluminium key alloy.

The aluminium-copper-zinc alloys have largely superseded the simple aluminium-zinc alloys, since the addition of small percentages of copper inhibits to a great extent the falling off of the mechanical strength at high temperatures and has no adverse effect on the machinability, while it improves the casting properties. The alloys containing 2–3% copper and 10–14% zinc are the chief representatives of this group in commercial use. A British Aircraft Specification **L5** exists for an alloy of this type and similar compositions are utilised very generally on the Continent and in America (in the latter country about 1% of iron is usually added).

Silicon is probably second in importance to copper as a constituent of an alloy, principally on account of its influence on the process of casting: it increases fluidity for pouring and reduces shrinkage and porosity. In the binary alloys (which are lighter than pure aluminium and considerably lighter than aluminium-copper or aluminium-zinc alloys) the tensile strength increases with increasing silicon content, rapidly up to 5% and then more gradually up to a maximum at 11%. An important property of the silicon alloys is their ability to underg
" modification " by small percentages of sod
or certain other elements : the usual effe
refine the structure with an impro
mechanical properties.

The modification process is carr
cipally on the alloys with higher silicon
from 8 to 15%—known under trade
as *Alpax* and *Wilmil*, which are
different countries. A British A
tion **L33** covers the 12% s
modified condition. In A
containing casting alloys

sede the copper- and copper-zinc-containing alloys for general purposes.

The binary aluminium-silicon alloys are comparatively soft and accordingly other hardening elements are frequently introduced.

Magnesium has a limited use in straight binary casting alloys containing up to 10% magnesium. The aluminium-magnesium alloys are again lighter than pure aluminium. Magnesium is, however, principally important as an alloying addition in conjunction with silicon and reference to this is made below.

Manganese.—A binary alloy containing 2% manganese has been used to some extent in the United States on account of its good corrosion resistance, but it has rather poor casting properties.

Other Alloys.—There are several important special casting alloys which may be briefly referred to. The well-known **RR** alloys are a group of complex alloys containing small additions of copper, nickel, magnesium, iron, titanium, and silicon ; " **Y** " alloy contains copper, nickel, and magnesium ; **K.S.** *Seewasser* alloy (developed for sea-water corrosion-resistance, as its name implies) contains magnesium, manganese, and antimony. Certain alloys have been developed primarily for pistons on account of their low heat expansion ; these have usually silicon as the principal alloying constituent with additions of such elements as copper and nickel as hardeners.

Heat Treatment.—Before giving an account of the light forging alloys, heat treatment comes into consideration. Reference has already been made to the fact that the solid solubility of copper-aluminium decreases with decrease of temperature : with several elements aluminium possesses the capacity for forming solid solutions whose maximum concentrations decrease with temperature. This fact makes it possible, in accordance with the now generally accepted hypothesis, to greatly increase the hardness and strength of the alloys by controlling the distribution of the soluble constituents and the precipitation of particles of specifically hard substances such as $CuAl_2$, Mg_2Si, and $FeAl_3$. In practice the effect is obtained by heating an alloy containing the appropriate element to a temperature within the solid solution region of the equilibrium diagram and beyond the boundary between this phase and the region in which a stable precipitate occurs ; followed by quenching the solid solution rapidly enough to obta
state of supersaturation, retarding the
pr
ation of the compound. Finally, pre-
on of the compound is obtained under
lled conditions of time and temperature
led " ageing "), the ultimate strength and
ess of the alloy depending up to a certain
al limit on the size and dispersion of the
cles of the compound.

he classical example of an alloy of this type
uralumin—a name which in reality covers a
of alloys containing copper, magnesium
nganese, of which the most common com-
is about 4% Cu, 0·5% Mg, and 0·5%
loped by A. Wilm. When an alloy
composition (which ordinarily has a
h of about 42,000 lb. per sq. in.)

is heated to 500°C. for a sufficient length of time, all the $CuAl_2$ compound goes into solid solution in aluminium : by quenching rapidly the $CuAl_2$ is not immediately precipitated, but with lapse of time (at ordinary temperatures in the case of duralumin) particles of this compound, of microscopic dimensions, are precipitated and the tensile strength becomes about 60,000 lb. per sq. in. Various theories have been advanced by the physical metallurgists to account for this increase in strength due to the presence of the finely disseminated hard $CuAl_2$ particles.

The precipitation theory outlined above gives a consistent explanation of the observed phenomena in the aluminium alloys where the necessary solubility relations hold, and it has, moreover, received support from the observations made on certain heavy and ferrous alloys and appears capable of generalisation.

In the duralumin alloys there are actually two hardening agents, the compound $CuAl_2$ and the compound Mg_2Si, and the solubility relations are complex and rendered more so by the presence of other alloying elements.

The silicides of magnesium, calcium, lithium, and zinc, and compounds of antimony-magnesium, aluminium-nickel, aluminium-zinc, and aluminium-zinc-magnesium are also substances which can act as hardening agents in aluminium alloys, rendering them heat-treatable.

The ageing part of the process of heat treatment allows of control of the rate of hardening, which can, for instance, be delayed by reducing the temperature (ice storage) or, in some instances, accelerated by raising the (ageing) temperature.

The discovery of the heat-treatability of the light aluminium alloys has been of immense importance in contributing to their development as strong constructional alloys. The technique of heat treatment has been very greatly advanced since Wilm's work before the War. Heat treatment is of primary importance in the wrought form of light alloys, but it is applicable in the case of a few casting alloys, notable examples being the **RR** alloys and "**Y**" alloy.

Forging Alloys.—The forging alloys rarely contain more than 6% of added elements and generally less.

A number of forging alloys are used without heat treatment, since certain alloying constituents increase the capacity for hardening under cold work and rolled sheet of mo tely high tensile strength (of the order of 15 t er sq. in.) can be obtained without heat-trea Manganese is one of these elements and small percentages of manganese (1–2%) of work-hardening. The aluminium-s alloys with 5–7% silicon may also be r Alloys with low percentages of added copp nickel and alloys of aluminium, manga and copper have found a limited comme use. The binary alloys of zinc with 1 zinc also formerly found some use for forging. The heat-treatable alloys, far outweigh in importance this small alloys for wrought forms.

Duralumin has been briefly refe

preceding section. It may be considered the most important as well as the ***doyen*** of the strong light alloys for forging. The physical properties of this alloy are summarised below :

Specific gravity, 2·79.
Specific heat, 0·214.
Thermal conductivity, 31. (compared with silver, 100).
Electrical conductivity, 41 (compared with copper, 100).
Coefficient of linear expansion, 0·000023 per °C. (20°–100°C.).
Young's Modulus, 10×10^6 lb. per sq. in.
Brinell hardness (heat treated), up to 110.

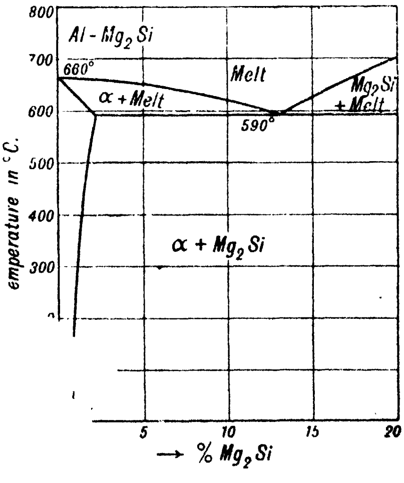
Duralumin is non-magnetic, takes a good polish, and in the annealed condition can be drawn, spun, formed, and stamped. To some extent the alloy loses its hardness at high temperatures.

From the figures for the mechanical properties it may be seen that weight for weight duralumin is about three times as strong as mild steel ; and it can and does compete with the structural steels.

A number of variants of duralumin containing additional alloying elements have been developed for special purposes and are known under trade names.

"*Y*" *alloy* is an alloy somewhat of the duralumin type, containing, besides 4% **Cu** and 1½% **Mg**, 2% **Ni**, which often is used for forging as well as casting. It differs from duralumin in its hardening properties with heat treatment, since the presence of nickel leads to the formation of a ternary **Cu-Ni-Al** compound and $CuAl_2$ is not formed, hardening being due to Mg_2Si only. The equilibrium relations of the ternary compound are complex. The alloy retains its strength at high temperatures to a greater degree than duralumin.

The *aluminium-magnesium-silicide alloys* are another group of valuable forging alloys which



much by reason of their on heat treatment as because of other properties, such as exceptional ductility. In the case of these alloys spontaneous hardening at ordinary temperatures does not occur after quenching, a second heating (artificial ageing) being required, and this fact is of importance in the working of the alloys.

" Plated " Alloys.—An interesting development in light alloys is the production of strong light alloy sheet with an integral plated coating, rolled on under pressure, of pure aluminium or of a second alloy possessed of special properties, to increase corrosion resistance (*see* below). Products of this type are known as *Alclad* (in America), *Aldural* (in this country), etc.

A list of the trade names of some of the better known light aluminium alloys not referred to in the foregoing summary is given below, with indications of the compositions.

Properties of the Aluminium Light Alloys.—The outstanding property of the aluminium alloys is, of course, their lightness, but the possibility of saving weight by their use depends also in most cases on their mechanical properties, that is to say, on their behaviour under stress. The tensile strength, hardness and ductility are the most commonly considered factors : the following table shows these properties for a few typical light alloys, both casting and forging alloys. (In the former the figures for chill or die castings are seen to be somewhat higher than in the same alloys cast in sand.)

The heat-treated light alloys which combine strength and ductility also have a very useful impact resistance and withstand repeated impact. The fatigue limit of the cast aluminium alloys is of the same order of magnitude as that

Alloy.	Nature of Alloy.	Country of Origin.	Percentage of Alloying Elements.
Aeral	Casting Alloy	France	Cu 4·5%, Mg 1·2%, Mn 0·25%, Cd 1–2%.
Aldrey	Forging Alloy	Switzerland	Si 0·5–0·6%, Mg 0·4–1%.
" American Alloy "	Casting Alloy	U.S.A.	Cu 8%.
Anticorodal	Casting and Forging Alloy	Switzerland	Si 1–2%, Mg 0·65%, Mn 0·7%.
Avional	Forging Alloy	Switzerland	Cu 3·8%, Mg 0·55%, Mn 0·5%.
Birmabright	Forging and Casting Alloy	England	Mg 3·5%, Mn 0·5%.
Birmasil	Casting Alloy	England	Si 10–13%.
Bohnalite	Piston Alloy	U.S.A.	Si 0·4%, Cu 10%, Mg 0·5%.
Ceralumin	Casting Alloy	England	Si 1·2%, Cu 2·5%, Mg 0·8%, Ni 1·5%, Ce 0·15%.
" German Alloy "	Casting Alloy	Germany	Cu 2–3%, Zn 10–12%.
Hiduminium	(RR and " Y " Alloys)		
Hydronalium	Forging and Casting Alloy	Germany	Si 0·2–1·5%, Mg 5–12%, Mn 0·2–0·5%.
Kolchugalumin	Forging Alloy	U.S.S.R.	Nickel-containing Duralumin.
Lautal	Forging Alloy	Germany	Si 1%, Cu 4·4–5·5%.
Lo-Ex	Piston Alloy	U.S.A.	Si 14%, Cu 0·8–0·9%, Mg 1%, Ni 2·5%, Fe 1%.
Magnalium	(Old) Casting Alloy	Germany	Mg 3–15%.
Mg-7	Forging Alloy	England	Mg 6·5–7·25%, Mn 0·30–0·60%.
Pantal	Forging Alloy	Germany	Si 0·5–1%, Mg 0·8–2%, Mn 0·4–1·4%, Ti 0·3%.
Silumin	Casting Alloy	Germany	Si 12–13·5%.
Wilmil	Casting Alloy	England	Si 10–13%.

	Condition.	Minimum Tensile Strength lbs./sq. in.	Minimum Elongation. %	Brinell Hardness No.
Casting Alloys—				
8% Copper Alloy	Sand cast	17,000	1·5	65
	Chill cast	20,000	3·0	—
12% Silicon Alloy (modified)	Sand cast	24,000	5·0	50
RR 53	Sand cast and heat-treated	36,000	—	—
	Chill cast and heat-treated	45,000	—	130
Forging Alloys—				
Duralumin	Sheet heat-treated	56,000	8–15	105
" Y " Alloy	Sheet heat-treated	52,000	8–15	—
Mg_2Si Alloy	Sheet heat-treated	50,000	20–25	100

of cast-iron (up to *ca.* 12,000 lb. per sq. in. measured by the rotating beam), while the magnesium-containing alloys and the heat-treated duralumin type of alloy in the wrought form have a very considerably higher fatigue strength.

In addition to their favourable mechanical and working properties, many of the aluminium alloys have other valuable qualities. The alloys with small percentages of magnesium and silicon have, on suitable heat treatment, an electrical conductivity remarkably high among alloys, which is little less (about 10%) than that of pure aluminium, while the gain in tensile strength, of the order of 100%, renders these alloys specially valuable for electrical conductor applications. The alloys with small additions of magnesium, silver, or silicon have very good optical properties, having a high reflectivity, and practically all the alloys are possessed of good heat conductivity. The silicon alloys have a particularly low coefficient of expansion (down to $19{\cdot}2\times10^{-6}$ per °C.).

Corrosion Resistance.—One of the most important considerations in many of the practical applications of metals is their corrosion resistance and in this respect the light aluminium alloys are in a favourable position. They share with pure aluminium the ability to form an adhering, tenuous, and impervious surface film which protects them against corrosion, but as would be expected, they are nevertheless in general inferior to the pure metal in their actual corrosion resistance. Some alloying constituents, however, have only a slight effect in this direction, *e.g.* antimony and manganese, these elements are found in special alloys and the latter element may even improve the corrosion resistance of commercial grades of aluminium. Among the cast alloys those with additions of the heavy elements such as copper and zinc have the lowest resistance, while the silicon alloys behave very well even under severe service conditions. The manganese binary alloy is the best from the point of view of corrosion resistance, but it is not a very good foundry alloy and is rather soft. Of the wrought alloys the manganese alloy is quite equal to commercial aluminium and in some cases superior.

Corrosion Protection.—In the case of most of the aluminium alloys the same method of protection as for the pure metal is available, namely, the provision of highly resistant coatings by anodic oxidation or chemical treatment. Magnesium-silicon-, magnesium- and manganese-containing alloys are specially amenable to such protection. In the presence of higher percentages of heavy metals such as copper or zinc surface treatment becomes difficult, but reference has been made above to the mechanical plating of pure aluminium or corrosion-resistant light alloys on the surface of the wrought alloys of this type.

Anodic Oxidation.—The preceding paragraph mentions the applicability of surface coatings to the aluminium alloys. By far the most important of these are the oxide coatings which are produced on those of the alloys which do not contain high percentages of heavy alloying constituents when they are made the anode in a weakly acid or alkaline electrolyte. The electrolytes most commonly used are sulphuric acid, oxalic acid and chromic acid. The anodic oxide films are enduring and their thickness, hardness and physical properties can be controlled: they can be dyed to any colour with organic or, in some cases, inorganic dyes, and can be printed on by colour or, after sensitisation, by photographic processes.

Applications of the Light Aluminium Alloys.—The light aluminium alloys have a remarkably wide field of application, since they include among their various composition formulæ many of the most desirable properties of metals, and can, by virtue of anodic oxidation, be given the appearance and some of the attributes of non-metallic materials. They enter at the one end of the scale into the structural engineering field and at the other into the manufacture of such a variety of small objects, as kitchen utensils, hardware, cosmetic containers, and buttons. Bridge floors have been constructed of aluminium alloy and nearly every type of small machine part, *e.g.* for the textile industry, exists in light alloy. In transportation they are ubiquitous—the initiant of modern aircraft, they are now established as constructional materials in rail and road transport units and even for marine use. In the electrical field their use ranges from overhead transmission lines to wireless accessories. The optical properties of certain of the alloys fit them for use as reflectors; the good thermal properties of others have given them a wide use as pistons. In architecture and in furniture aluminium alloys, both plain and anodised (often dyed), are quite familiar. In the chemical and food industries the corrosion-resistant alloys are widely used as containers, *e.g.* for brewery vats, milk plant, containers for heavy chemicals, resins and varnishes, fats and oils, glue and gelatine; for plant in the bleaching and dyeing, rubber, paper, and leather industries, and for water distribution and sewage. They are coming into use for pressure vessels for gas.

British Standard Specifications Relating to Light Aluminium Alloys.—The following list shows the British Standard Specifications relating to light aluminium alloys current at 1st April, 1936:

I. *B.S.I. Standards.*

361 (1929): 7% Copper-Aluminium Alloy Castings for General Engineering Purposes.

362 (1929): 12% Copper-Aluminium Alloy Castings for General Engineering Purposes.

363 (1929): Zinc-Copper-Aluminium Alloy Castings (Suitable for Crankcases and General Use) (13·5–2·75% approx.).

395 (1930): Wrought Light Aluminium Alloy Sheets and Strips for General Engineering Purposes (Heat-treated Duralumin).

396 (1930): Wrought Light Aluminium Alloy Tubes for General Engineering Purposes (Heat-treated Duralumin).

414 (1931): Wrought Light Aluminium Alloy Sheets and Strips for General Engineering Purposes (Heat-treated "Y" Alloy).

477 (1933): Wrought Light Aluminium Alloy Bars for General Engineering Purposes (Duralumin as Wrought or Heat-treated).

478 (1933) : Wrought "Y" Alloy Bars for General Engineering Purposes (as Wrought or Heat-treated).

532 (1934) : Light Aluminium Alloy Forgings for General Engineering Purposes (Duralumin Heat-treated, Annealed, or as Forged).

533 (1934) : "Y" Alloy Forgings for General Engineering Purposes (Heat-treated, Annealed, or as Forged).

II. *Standard Specifications for Aircraft Materials.*

4L.1 (1935) : Wrought Light Aluminium Alloy Bars, Extruded Sections and Forgings (Heat-treated Duralumin).

3L.3 (1929) : Wrought Light Aluminium Alloy Sheets and Strips (Heat-treated Duralumin).

3L.5 (1933) : Aluminium-Zinc-Copper Alloy Castings (13·5–2·75% approx.).

3L.8. (1933) : 12% Copper-Aluminium Alloy Castings.

4L.11 (1933) : 7/1 Aluminium Alloy Castings (**Cu, Sn** Optional).

2L.24 (1933) : "Y" Aluminium Alloy Castings (Not Heat-treated).

3L.25 (1935) : Aluminium Alloy Bars and Forgings (including Pistons other than Drop-forged) ("Y" Alloy).

L.33 (1933) : Silicon-Aluminium Alloy Castings (11½% approx.).

L.35 (1933) : "Y" Aluminium Alloy Castings (Heat-treated).

L.39 (1935) : Aluminium Alloy Bars for Machining (3 to 6 inches) (Heat-treated Duralumin).

L 42 (1935) : Aluminium Alloy Drop forgings, including Pistons and Cylinder Heads (Heat-treated RR 59).

L.43 (1935) : Aluminium Alloy Drop-forgings for Pistons and Cylinder Heads (Heat-treated "Y" Alloy).

3T.4 (1928) : Wrought Light Aluminium Alloy Tubes (Heat-treated Duralumin).

MAGNESIUM ALLOYS.

Magnesium alloys with the majority of metals, forming compounds with most of these. Iron, cobalt, chromium, and beryllium do not form alloys with magnesium and manganese and the alkali metals only alloy over a limited composition range.

The magnesium-rich alloys as a rule contain less than 12% of added elements.

The magnesium-aluminium series is the most important. These alloys exhibit limited solid solubility and form a globular eutectic : they are possessed of high tensile strength (of the order of 14,000 lb. per sq. in. for castings and 26,000 lb. per sq. in. for forgings) and medium hardness (of the order of 60 Brinell). The commercial magnesium aluminium alloys usually have small additions of manganese and/or zinc, and for special purposes such elements as cadmium, silicon and cerium may be added. The magnesium-aluminium alloys are capable of heat treatment, the hardening constituent being Al_2Mg_3.

The magnesium-zinc series is similar to magnesium-aluminium. Cadmium forms a solid solution with magnesium, the binary alloys having only moderate strength and low hardness, but being readily forgeable. The magnesium-copper, magnesium-nickel and magnesium tin series exhibit little or no solid solubility and form lamellar eutectics. The binary alloys of these series are little used because of their poor corrosion resistance. The other alloys of magnesium have an unexpectedly good corrosion resistance, but for continued exposure to marine conditions it is necessary to supply a protective surface treatment. Two processes have been worked out in this country. One of these depends on chemical treatment with selenious acid, which gives rise to a thin layer of magnesium selenide, and this is decomposed by water penetrating the pores to give hydrogen selenide, which reacts with oxygen to give a sealing deposit of selenium. The other method uses chromates or dichromates and is again a chemical treatment. In Germany attention has chiefly been paid to electrolytic treatment with fluorides, which is claimed to have special advantages over the other methods.

Commercial Nomenclature.—The magnesium-rich alloys have been given the generic name of *Dowmetal* in America. In Germany *Elektron* was originally introduced to cover the magnesium alloys with aluminium as principal alloying constituent and this significance is usual in this country, although the term "Elektron" is also frequently loosely used to mean any light alloy of magnesium. *Magnuminium* is a British trade name for **Mg Al-Zn-Mn** alloys.

The following table shows the compositions of the magnesium-base alloys which are covered by D.T.D. Specifications (which serve as a basis for inspection of materials not covered by existing British Standard Specifications) :

Specification, Dept. Tech. Dev. (D.T.D.), Air Ministry.	Aluminium, Max.	Zinc, Max.	Manganese, Max	Impurities, Max
59A (Castings)	8·5	3·5	0·5	1·7
88B (Forgings)	11·0	1·5	1·0	1·5
118 (Sheet)	0·2	0·2	2·5	(1·1)*
136A (Pressure Castings)	11·0	3·5	0·5	1·5
140A (Castings)	0·2	0·2	2·5	(1·1)*
142 (Bars)	0·2	0·2	2·5	(1·1)*
259 (Bars)	11·0	1·5	1·0	1·5

* Includes **Cu** and **Si** which in the earlier Specifications were listed separately but later included as impurities.

Properties and Applications.—The most outstanding characteristic of the magnesium alloys is their lightness: magnesium alloy castings in common use have only one quarter the weight of iron castings. The tensile properties of the magnesium alloys are moderately high, but their elastic properties are rather poor. The alloys can be extruded and rolled with advantage to their mechanical properties. The aircraft industry is the largest user of magnesium alloy parts, although they are being adopted to some extent for industrial applications where their ultra-lightness is of value. Magnesium alloys in the mass are not liable to burn. F. H.

ALLYL. A univalent radicle C_3H_5—, or $CH_2:CH{\cdot}CH_2$—, isomeric with *propenyl* (*crotonyl*) $CH_3{\cdot}CH:CH$—.

Allyl acetate $CH_3{\cdot}CO_2C_3H_5$ boils at 103°–104°/733·9 mm. (Brühl), and has sp.gr. 0·9376 at 0° (Schiff). It is only slightly soluble in water, and has a rather sharp smell. It is prepared by the action of allyl iodide on silver acetate (Zinin, Annalen, 1855, **96**, 361; Cahours and Hofmann, Annalen, 1857, **102**, 295; Brühl, Annalen, 1880, **200**, 179; Schiff, Annalen, 1883, **220**, 109).

Allylacetic acid $C_3H_5{\cdot}CH_2{\cdot}CO_2H$, b.p. 187°–189°, d^{15} 0·98416 (Perkin), is slightly soluble in water and its smell resembles that of valeric acid. It is unaffected by reduction with sodium amalgam, but readily unites with two atoms of bromine. It is prepared by hydrolysing ethyl acetoallylacetate with dry sodium ethoxide, or by heating allylmalonic acid (Zeidler, Annalen, 1877, **187**, 39; Conrad and Bischoff, Annalen, 1880, **204**, 170; Henry, Chem. Zentr. 1898, ii, 663). The *chloride* $C_3H_5{\cdot}CH_2{\cdot}COCl$ is a thick, pungent-smelling syrup, b.p. 128°/765 mm., d^{16} 1·0739 (Henry, *l.c.*). Linstead and Rydon (J.C.S. 1933, 580) have shown that when allylacetic acid is treated with cold concentrated sulphuric acid, γ-valerolactone is produced. The acid in hexane solution adds on the elements of hydrobromic acid to give δ-bromohexoic acid, while if treated without diluent the γ-form is produced (*idem*, Nature, 1933, **132**, 643).

Allylacetone $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_3H_5$, b.p. 128°–130°, d^{27} 0·834, is an unpleasant-smelling liquid. It forms an amorphous compound with sodium bisulphite, and is reduced by sodium amalgam to hexenyl alcohol. It is prepared by hydrolysing ethyl acetoallylacetate (70 grms.) with crystallised baryta (215 grms.) and water (1,650 c.c.) (Zeidler, Annalen, 1877, **187**, 35; Merling, Annalen, 1891, **264**, 323). Treated with hydroxylamine it yields *allylacetoxime* $CH_3{\cdot}C(:NOH){\cdot}CH_2{\cdot}C_3H_5$, a liquid, b.p. 188° (corr.), soluble in alcohol, benzene, ether, acids, and alkalis.

Allylacetylene is obtained in 75% yield when magnesium acetylide is treated at −10° with allyl bromide (Grignard, Compt. rend. 1928, **187**, 517). It is a liquid, b.p. 41–42°, d^{22} 0·777. It is also formed when sodium acetylide is treated with allyl halide in liquid ammonia (Léspieaux, *see* A. 1928, 1233).

Allyl alcohol $CH_2:CH{\cdot}CH_2{\cdot}OH$ occurs to the extent of about 0·2% in raw wood spirit (Aronheim, Ber. 1874, **7**, 1381; Rubin and Medvedev, J. Appl. Chem. Russ. 1933, **6**, 311). It is a pungent liquid with burning taste and is somewhat lachrymatory. It mixes readily with alcohol, ether, and water. It boils at 96·6° (corr.), and has d^{25}_{25} 0·8573 (T. E. Thorpe, J.C.S. 1880, **37**, 208).

Allyl alcohol is prepared by distilling a mixture of glycerol and formic acid (Organic Syntheses, 1921, **1**, 15; 1926, **6**, 103; Dewael, Bull. Soc. chim. Belg. 1930, **39**, 40; Delaby and Dubois, Compt. rend. 1928, **187**, 949; 1929, **188**, 710), or by slow distillation with oxalic acid and a trace of ammonium chloride in place of the formic acid treatment (Chattaway, J.C.S. 1914, **105**, 151; 1915, **107**, 407; Coffey and Ward, *ibid.* 1921, **119**, 1301). The product from these preparations is an aqueous solution of the alcohol contaminated with formic acid. It is cautiously treated with potassium carbonate, which neutralises the acid and salts out the alcohol, and this is separated and distilled, using a column, to yield a fraction, b.p. up to 98°, containing about 70% of the alcohol. Of the various methods of dehydration described in the literature cited above, the one using successive treatments with potassium carbonate, potassium hydroxide, and quicklime has been found quite effective.

Allyl alcohol is oxidised by chromic acid solution to acrolein and formic acid; acid permanganate solution yields three molecules of formic acid, while with dilute nitric acid a mixture of formic and oxalic acids is produced. Addition products are obtained by reaction with chlorine, bromine, iodine chloride and cyanogen, while Wohl and Jaschinowski (Ber. 1921, **54** [B], 476) have described a method of brominating in which *N*-bromoacetamide is employed. The alcohol is partially reduced to propyl alcohol when boiled for several hours with zinc and dilute sulphuric acid. Farmer and Galley (J.C.S. 1933, 687) have studied quantitatively the hydrogen uptake in the presence of various catalysts (*see also* Pollit, Chem. Age, 1921, **5**, 88; Lebedev, J.C.S. 1925, **127**, 417).

The pyrolytic decomposition of allyl alcohol when passed over various heated metal oxides has been investigated by several workers and among the products, which vary according to conditions, are acrolein and propaldehyde, and propylene and ethylene (Sabatier and Gaudoin, Compt. rend. 1918, **166**, 1033; Weston and Adkins, J. Amer. Chem. Soc. 1928, **50**, 1930; Peytral, Bull. Soc. chim. 1921, [iv], **29**, 39; Sabatier and Kubota, Compt. rend. 1921, **173**, 17, 212).

The esterification constants of the alcohol with various acids have been determined by Skrabal and Zahorka (Monatsh. 1933, **63**, 1).

Detection and Estimation.—Denigès (Bull. Soc. chim. 1909, [iv], **5**, 878) describes the following colour reactions for the detection of allyl alcohol, depending on the formation of (1) glyceraldehyde and (2) dihydroxyacetone, and the condensation of these products with various reagents. Bromine water (0·6 c.c. in 100 c.c. water) is added to 0·1 c.c. of allyl alcohol, until a slight permanent coloration is produced, the liquid after boiling and cooling contains glyceraldehyde. To 0·4 c.c. of this liquid 0·1 c.c. of a 5% solution of codeine, resorcinol, thymol, or β-naphthol is added, followed by 2 c.c. of sulphuric acid (sp.gr. 1·84), and the mixture warmed during 3 or 4 minutes at 100°. Codeine and thymol give reddish-violet colorations, resorcinol wine-red, and β-naphthol yellow with greenish fluorescence. The second series of colour reactions is obtained by adding to the brominated liquid above described a further 5 c.c. of the bromine water, heating during 20 minutes at 100°, then boiling to remove excess of bromine and cooling. This liquid contains dihydroxyacetone, and in the presence of concentrated sulphuric acid gives a deep-blue colour with codeine, orange-red with resorcinol, blood-red with thymol, and green with green fluorescence with β-naphthol (Denigès, Bull. Soc. chim. 1909 [iv], **5**, 878).

Bromine is quantitatively absorbed by allyl alcohol, whether the former is in excess or not, and the reaction is suitable for the exact quantitative estimation of the alcohol, which may be effected either by direct titration with bromine water until a permanent yellow coloration is obtained, or by treating the acidified aqueous solution of the alcohol with an excess of bromide-bromate solution, followed by addition of potassium iodide and subsequent titration of the liberated iodine (Stritar, Monatsh. 1918, **39**, 617). Lappi (Anal. Asoc. Quím. Argentina, 1930, **18**, 43) uses bromine in carbon tetrachloride solution, the addition being carried out in the cold and dark.

Allylamines.

Monoallylamine $C_3H_5{\cdot}NH_2$, b.p. 53·3°, d^4 0·7799 and d^{15} 0·7688 (Perkin, J.C.S. 1889, **55**, 697); b.p. 58° and d^{15} 0·864 (Rinne, Annalen, 1873, **168**, 262); b.p. 56°–56·5°/756·2 mm. (Schiff, Ber. 1886, **19**, 565). It is prepared from allyl *iso*cyanate and potash, or from allyl iodide and ammonia, or by reduction of allyl mustard oil with zinc and hydrochloric acid (Oeser, Annalen, 1865, **134**, 8). It possesses a penetrating smell, which excites tears and produces sneezing. It is miscible with water in all proportions, and is a strong base, forming a crystalline platinichloride $(C_3H_5{\cdot}NH_2)_2PtCl_6$ and a sulphate $(C_3H_5{\cdot}NH_2)_2H_2SO_4$. The hydrochloride melts at 105°–110° (Delépine, Bull. Soc. chim. 1897 [iii], **17**, 294) and the picrate at 140°–141° after sintering (Gabriel and Eschenbach, Ber. 1897, **30**, 1125).

Diallylamine $(C_3H_5)_2NH$, b.p. 111°, is prepared from allylamine and allyl bromide (Ladenburg, Ber. 1881, **14**, 1879; Liebermann and Hagen, Ber. 1883, **16**, 1641).

Triallylamine $(C_3H_5)_3N$ is a very unpleasant-smelling liquid, b.p. 150°–151° (Pinner, Ber. 1879, **12**, 2054); 155°–156°, $d^{14\cdot3}$ 0·8094 (Zander, Annalen, 1882, **214**, 151). It is prepared by distilling tetra-allylammonium bromide with a large excess of recently fused potash (Grosheintz, Bull. Soc. chim. 1879 [ii], **31**, 391) or from allyl chloride and alcoholic potassium cyanide in the cold (Pinner, *l.c.*); or from allyl chloride and ammonia (Malbot, Bull. Soc. chim. 1888 [ii], **50**, 90). It is thrown out of aqueous solution by potash, and forms a crystalline platinichloride and a hydrochloride.

Tetra-allylammonium bromide $(C_3H_5)_4NBr$ is a crystalline solid, soluble in alcohol and water, but only slightly so in ether. It is prepared by passing ammonia into an alcoholic solution of allyl bromide. The product is purified by recrystallisation from alcohol containing a little ether (Grosheintz, Bull. Soc. chim. 1879 [ii], **31**, 390). Treated with moist silver oxide it yields tetra-allylammonium hydroxide.

Tetra-allylammonium iodide $(C_3H_5)_4NI$ is the main product of the reaction of allyl iodide on ammonia at the ordinary temperature (Cahours and Hofmann, Annalen, 1857, **102**, 305; Malbot, Ann. Chim. Phys. 1888 [vi], **13**, 488). It is a crystalline solid, insoluble in strong potash solution.

Allylaniline $C_6H_5{\cdot}NH{\cdot}C_3H_5$, b.p. 208°–209°, d^{25} 0·982, is a yellow oil produced by the action of allyl iodide on aniline or by treatment of sodium formanilide with allyl iodide or bromide (Dains and others, J. Amer. Chem. Soc. 1922, **44**, 2637). It has been shown that allyl bromide reacts with aniline to yield β-bromoallylaniline (v. Braun and Tauber, Annalen, 1927, **458**, 102; Schiff, Annalen Suppl. 1864–5, **3**, 364). It yields a p-*toluenesulphonyl* derivative, m.p. 69·3° (Carnahan and Hurd, J. Amer. Chem. Soc. 1930, **52**, 4586).

Diallylaniline $C_6H_5{\cdot}N(C_3H_5)_2$, b.p. 243·5°–245°, $d^{19\cdot8}$ 0·9538, prepared by heating aniline (1 mol.) and allyl bromide (1 mol.), separating the allylaniline and repeating the process (Zander, Annalen, 1882, **214**, 149).

Allyl benzene $C_6H_5{\cdot}CH_2{\cdot}CH : CH_2$ is obtained by heating benzene, allyl iodide, and zinc-dust at 100° (Chojnacki, Jahresber. 1873, 559; Fittig, Annalen, 1874, **172**, 312). It boils at 155°. The isomeric *propenyl benzene* or *a-phenylpropylene*—$C_6H_5{\cdot}CH : CH{\cdot}CH_3$ is sometimes incorrectly referred to as allyl benzene.

Allyl bromide, *γ-bromopropylene,*

$$CH_2 : CH{\cdot}CH_2Br$$

(Zander, Annalen, 1882, **214**, 144); b.p. 70·5° (corr.) (T. E. Thorpe), is formed by the action of phosphorus tribromide on allyl alcohol; or by dropping allyl alcohol into a hot solution of potassium bromide in sulphuric acid (1 vol. acid to 1 vol. H_2O) according to Grosheintz (Bull. Soc. chim. 1878 [ii], **30**, 78). It is most conveniently prepared from the solution of hydrobromic and sulphuric acids obtained by decolorising bromine with sulphur dioxide and treating this solution with the alcohol (Kamm and Marvel, J. Amer. Chem. Soc. 1920, **42**, 299; Organic Syntheses, 1921, **1**, 3).

Allyl bromide absorbs hydrogen bromide in bright light forming trimethylene bromide (αγ-dibromopropane); in the dark propylene dibromide (αβ-dibromopropane) is also produced (Holleman and Matthes, Proc. K. Akad. Wetensch. Amsterdam, 1918, **21**, 90; Wibaut, Rec. trav. chim. 1931, **50**, 313).

Allyl chloride $CH_2 : CH{\cdot}CH_2Cl$, b.p. 46°, d^0 0·9547 (Tollens, Annalen, 1870, **156**, 154); $d^{19\cdot3}$ 0·9371 (Zander, Annalen, 1882, **214**, 142); b.p. 45·29° (corr.) (T. E. Thorpe). It is obtained by the action of mercuric chloride on allyl iodide, or from allyl oxalate, calcium chloride, and alcohol at 100° (Oppenheim, Annalen, 1866, **140**, 205); by heating allyl alcohol and concentrated hydrochloric acid at 100° for some hours (Eltekow), or by passing propylene dichloride over calcium chloride heated to 300°–350° (U.S.P. 1477047). It may be prepared by passing a current of dry hydrogen chloride into allyl alcohol in which zinc chloride is present. Diallyl ether is formed as a by-product (Coffey and Ward, J.C.S. 1921, **119**, 1301). Dewael (Bull. Soc. chim. Belg. 1930, **39**, 40) uses a small amount of copper chloride as the catalyst. It combines with hydrogen chloride to form *propylene dichloride* $C_3H_6Cl_2$, and with fuming hydrobromic acid yielding α-chloro-γ-bromopropane $CH_2Cl{\cdot}CH_2{\cdot}CH_2Br$.

Allyl cyanamide, *sinamine*, $C_3H_5{\cdot}NH{\cdot}CN$, is produced by warming allyl thiocarbamide with lead hydroxide on the water-bath (Will, Annalen, 1844, **52**, 15). On standing for some months crystals separate from the resulting product. It is prepared by shaking an aqueous solution of allyl thiocarbamide with mercuric oxide until the solution no longer blackens ammoniacal silver nitrate (Andreasch, Monatsh. 1881, **2**, 780). It is alkaline in reaction, precipitating metallic oxides and replacing ammonia in its salts. The crystals contain $\frac{1}{2}H_2O$ and melt at 100°, giving up their water. It forms a difficultly crystallisable salt with oxalic acid, but not with other acids, and forms double compounds with mercuric and platinic chlorides.

Allyl cyanide, *vinylacetonitrile*, $C_3H_5{\cdot}CN$, b.p. 119° (corr.), d^0 0·8491 and d^{15} 0·8351. It is obtained by the action of allyl iodide on potassium cyanide, and, together with other products, by allowing allyl mustard oil (allyl *iso*thiocyanate, $C_3H_5{\cdot}NCS$) to remain in contact with water for some weeks, and also by the action of acetic anhydride on vinylacetaldoxime. It has been prepared by Henry (Chem. Zentr. 1898, ii, 662) by the action of phosphorus pentoxide on α- or β-hydroxy-butyronitrile, but is more conveniently obtained by treating aqueous allyl alcohol first with concentrated hydrochloric acid and then with a slight excess of cuprous cyanide (Breckpot, Bull. Soc. chim. Belg. 1930, **39**, 462; Falaise and Frognier, *ibid.* 1933, **42**, 427) or by refluxing equivalent quantities of allyl bromide and cuprous cyanide (Bruylants, *ibid.* 1922, **31**, 175). It is a liquid with an unpleasant, onion-like odour. On warming at 50°–60° with fuming hydrochloric acid for two hours, chlorobutyric acid is produced. Chromic acid oxidises it to acetic acid, and nitric acid to oxalic acid. If warmed for ½ hour with excess of 0·4% potassium hydroxide it is converted into the isomeric crotononitrile, while in the presence of sodium ethoxide it adds on the elements of ethyl alcohol to give ethoxybutyronitrile (Bruylants, Bull. Soc. chim. Belg. 1924, **33**, 331).

Allyl ether $C_3H_5{\cdot}O{\cdot}C_3H_5$, b.p. 94·3°, d^{18} 0·8046, is prepared from allyl iodide and sodium alloxide, or from allyl iodide and mercuric oxide (Cahours and Hofmann, Annalen, 1857, **102**, 290; Berthelot and Luca, Ann. Chim. Phys. 1856 [iii], **48**, 291), by treating allyl alcohol with 20% by vol. of $H_2SO_4{\cdot}3H_2O$ (Senderens, Compt. rend. 1925, **181**, 698); Gebauer-Fulnegg and Moffatt (J. Amer. Chem. Soc. 1934, **56**, 2009) claim a high yield by treating the alcohol with liquid hydrogen chloride.

Allyl ethyl ether $C_3H_5{\cdot}O{\cdot}C_2H_5$, b.p. 66°–67°/742·9 mm. (Brühl, Annalen, 1880, **200**, 178), is prepared from allyl iodide and sodium ethoxide.

Allyl iodide C_3H_5I, b.p. 102·79° (corr.) (Thorpe and Rodger, Phil. Trans. A. 1894, **185**, 379; 1897, **189**, 71), d_0^0 1·8696. Berthelot and Luca (Ann. Chim. Phys. 1855 [iii], **43**, 257) obtained it by the action of PI_3 on glycerol. It may be prepared by leaving together for 24 hours red phosphorus (20 grms.), allyl alcohol (160 grms.), and iodine (254 grms.) (Tollens and Henninger, Annalen, 1870, **156**, 156); or by the following process: 100 grms. of iodine and 1,500 grms. of carefully dehydrated glycerol are brought together in a large vessel, the air displaced by a current of carbon dioxide, and 300 grms. of yellow phosphorus gradually added. The allyl iodide is distilled off in a stream of carbon dioxide, and contains as impurity some *iso*propyl iodide. According to Rasik Lal Datta (J. Amer. Chem. Soc. 1914, **36**, 1005) the use of carbon dioxide is unnecessary. It is purified by dissolving it in alcohol and shaking with mercury, when the compound HgC_3H_5I is precipitated. This is recrystallised from water and decomposed, regenerating allyl iodide, by distilling with water containing one equivalent of iodine (Linnemann, Annalen Suppl. 1864–5, **3**, 263). It reacts with bromine to form tribromhydrin, and with hydriodic acid to give diiodopropane. By long heating with about 20 parts of water it is converted into allyl alcohol and hydriodic acid.

Allylmalonic acid is obtained by alkaline hydrolysis of the ethyl ester, b.p. 108°–110°/16 mm., prepared by treatment of ethyl sodiomalonate with allyl bromide (Paul, Ann. Chim. 1932, [x], **18**, 303). It is decomposed at 160°–200° to yield allylacetic acid and carbon dioxide.

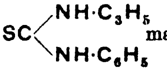
Allyl mercaptan $C_3H_5{\cdot}SH$, b.p. 90°, is obtained when allyl iodide is treated with potassium hydrosulphide, but better when dithioallylurethane $H_2N{\cdot}CS_2{\cdot}C_3H_5$ is heated (v. Braun, Ber. 1926, **59** [B], 1202). It decomposes slowly on distillation to yield the sulphide and H_2S. With mercuric chloride it yields $C_3H_5{\cdot}SHgCl$, which crystallises from alcohol in plates (Hofmann and Cahours, Annalen, 1857, **102**, 292; Gerlich, Annalen, 1875, **178**, 88).

A compound is prepared by passing a current of formaldehyde gas through glycerol (1 kilo) and allyl *iso*thiocyanate (5 grms.) heated to 190° until the weight of the whole is 1,400 grms. When cool the product is filtered and used as an antiseptic (Piot, F.P. 330988, 1903).

Allyl mustard oil (allyl *iso*thiocyanate, $C_3H_5{\cdot}NCS$) *v.* MUSTARD OIL and ESSENTIAL OILS.

Allyl nitrite $C_3H_5{\cdot}O{\cdot}NO$, b.p. 43·5°–44·5°,

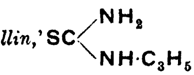
d^0 0·9546, is obtained by adding glycerol trinitrite to ice-cold allyl alcohol and cautiously distilling off the allyl ester (Bertoni, Gazzetta, 1885, **15**, 364). It is readily decomposed by shaking with water, and yields ethyl nitrite on treatment with ethyl alcohol.

Allyl-phenyl-thiourea  $SC\begin{cases}NH\cdot C_3H_5\\NH\cdot C_6H_5\end{cases}$ may be prepared from aniline and mustard oil (Zinin, Annalen, 1852, **84**, 348); or from allylamine and phenyl mustard oil (Weith, Ber. 1875, **8**, 1529). It forms monoclinic crystals, melting at 98°, and is readily soluble in ether, but not in water.

Allyl pyrrol $C_4H_4N\cdot C_3H_5$ is readily obtained by the action of allyl bromide on potassium pyrrol in ether (Ciamician and Dennstedt, Ber. 1882, **15**, 2581). It is a light-yellow oil, b.p. 105°/48 mm., turning brown on exposure to air. It is insoluble in water, but dissolves in HCl, producing a red colour.

Allyl sulphate $C_3H_5\cdot HSO_4$. The barium salt is prepared by adding allyl alcohol (1 vol.) to sulphuric acid diluted with its own volume of water (1 vol.) and leaving at ordinary temperatures for five days. Subsequently the mixture is heated to 70° for 12 hours, diluted with water (10 vols.), and saturated with barium carbonate (Szymanski, Annalen, 1885, **208**, 44; *v.* also Cahours and Hofmann, Annalen, 1857, **102**, 293). It forms characteristic salts, a number of which are described by Szymanski (*l.c.*).

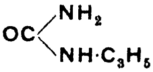
Allyl sulphide, *oil of garlic* (Ger. *Knoblauchöl*) $(C_3H_5)_2S$, b.p. 138·6°, $d_4^{26\cdot8}$ 0·88765, occurs in garlic (*Allium sativum*) and other plants. It is prepared from mustard oil and potassium sulphide at 100° (Wertheim, Annalen, 1847, **55**, 297); or from allyl iodide and potassium sulphide (Hofmann and Cahours, Annalen, 1857, **102**, 291). It has a very strong odour of garlic and is only slightly soluble in water.

Allyl thiocarbamide, *allyl thiourea*, *thiosinamine*, '*Rhodallin*,'  $SC\begin{cases}NH_2\\NH\cdot C_3H_5\end{cases}$, is produced by the prolonged action of aqueous ammonia on mustard oil (Dumas and Pelouze, Annalen, 1834, **10**, 326). It forms clear six-sided tables, which melt at 78·4°, after sintering at 71°. It is insoluble in benzene, sparingly soluble in water, and readily so in alcohol and ether. It combines directly with halogens, cyanogen, ethyl iodide, acids, etc. Mercuric oxide or lead oxide remove the elements of hydrogen sulphide yielding *sinamine* (allyl cyanamide),

$$C_3H_5\cdot NH\cdot CN.$$

On treatment with uranyl nitrite it yields allyl thiocyanate and ammonia. It has been used in surgery for the removal of scar tissue, being injected as a 10 or 15% solution in dilute glycerol, and also finds use as a sensitiser for photographic emulsions (Schmidt, Phot. Ind. 1926, 1016).

Allyl tribromide, *Tribromhydrin*, $C_3H_5Br_3$, is a slightly yellow liquid, b.p. 217°, $d^{15\cdot5}$ 2·430, and was obtained by Wurtz by treating allyl iodide with bromine, and by Berthelot and Luca by the action of phosphorus tri- and pentabromides on glycerol. It is a strong sedative and anodyne.

Allyl urea  $OC\begin{cases}NH_2\\NH\cdot C_3H_5\end{cases}$ crystallises in needles, melting at 85° (Cahours and Hofmann, Annalen, 1857, **102**, 299; Andreasch, Monatsh. 1884, **5**, 36). E. G. N.

ALLYLENE *v.* ACETYLENES.

ALMANDINE. A deep red garnet, often with a violet tinge (*v.* GARNET).

ALMOND. The kernel of the fruit of *Prunus amygdalis* (Stokes) [*Amygdalis communis* (Linn.)]. Two varieties occur in commerce, viz. the sweet (var. *dulcis*) and the bitter almond (var. *amara*). The primary difference between these lies in the larger proportion of the glucoside *amygdalin* present in the latter variety (2–3%). The enzyme *emulsin* present in the nuts converts amygdalin into a mixture of glucose, benzaldehyde, and hydrocyanic acid:

$$C_{20}H_{27}NO_{11}+2H_2O = C_6H_5\cdot CHO+HCN+2C_6H_{12}O_6$$

Almond oil consists largely of olein. This is extracted by pressure, and the press-cake is mashed with water until decomposition of amygdalin is complete. Steam distillation yields "oil of bitter almonds," containing 3% of hydrocyanic acid, which is separated by redistillation after the addition of sodium sulphite.

Analyses recorded by C. V. Hart (Ind. Eng. Chem. 1930, **22**, 1128) show the dry matter of almonds to contain:

	American Varieties.	Mediterranean Varieties.
Fat	55·3–58·7	57·0–59·6
Nitrogen	3·5–4·1	3·2–3·9
Sucrose	4·4–4·7	3·2–4·8
Pentosans	3·4–3·8	3·1–3·4
Ash	3·4–3·5	2·9–3·4
Hemicellulose	4·0–8·7	5·3–8·0

COMPOSITION OF ASH.

	American Varieties.	Mediterranean Varieties.
SiO_2	0·14–1·15	0·12–0·23
Fe_2O_3	0·27–0·37	0·30–0·54
CaO	11·9–14·6	6·7–11·4
MgO	13·6–14·7	13·6–14·9
P_2O_5	33·2–39·7	38·9–40·2
Na_2O	1·45–3·98	2·12–3·23
K_2O	23·9–27·7	24·7–27·0
SO_3	2·62–3·85	2·24–3·29
CO_2	3·86–4·15	3·01–5·22

In Crimean varieties high fat contents are usually associated with low proportions of protein; 48% of the ash consists of P_2O_5.

During the growth and maturation of almonds oil formation appears to occur at the expense of starch, sucrose, and glucose.

The commercial kernels are blanched either by scalding at 180°–200° F. for 3–5 minutes and rubbing off the skins or by alternate dipping in dilute sulphuric acid and in solutions of bleaching powder.

Common almond products have the following composition :

	Water.	Protein.	Fat.	Carbo-hydrate.	Ash.
Almond paste	34·2	13·4	23·9	33·4	1·6
Almond butter	1·7	22·2	61·5	11·8	3·0

Salted almonds contain approximately 2% of sodium chloride. A. G. Po.

ALMOND OIL is the fatty (fixed) oil obtained from the kernels of the bitter almond, *Prunus amygdalus*, var. *amara* (Stokes), and the sweet almond, *P. amygdalus*, var. *dulcis* (Stokes). The almond tree appears to have been indigenous to Turkestan and Middle Asia, but has been transplanted and cultivated extensively in the countries bordering on the Mediterranean Sea. Commercial almond oil is expressed chiefly from bitter almonds, which may be admixed with varying amounts of sweet almonds ; the latter, however, are rarely used alone for the preparation of the oil. Besides the fixed oil, bitter almonds contain a glucoside, *amygdalin*, which is hydrolysed by water in the presence of the ferment *emulsin* (which also occurs in the almond kernel) yielding benzaldehyde, dextrose, and hydrocyanic acid ; hence the press-cakes from the expression of fatty almond oil find a profitable outlet in the manufacture of *ethereal oil of bitter almonds*, which is prepared by steam distillation from the expressed meal.

Sweet almonds contain from 45–67% (average 59%), and bitter almonds from 35·5–62·5% (average 51·5%) of oil (Rosenthaler, Ber. pharm. Ges. 1922, 32, 237) ; on the commercial scale, yields of 44–55% and 38–45% of oil are obtained for the two varieties respectively. The pale-yellow, bland oils from the two varieties show no characteristic difference ; the oil, d^{15} 0·915–0·920, becomes turbid at temperatures below 10°C., and congeals at about −20°C. The saponification value of the oil ranges from 188–196, and the iodine value lies, as a rule, between 93 and 100, but exceptional values up to 104–105 have been recorded; almond oil conforming to the requirements of the British Pharmacopœia, 1932 Ed., for *Oleum amygdalæ Ang.*[1] must have an iodine value between 95 and 100.

The fatty acids of almond oil contain about 3–7·5% of saturated acids consisting chiefly of palmitic acid (*cf.* Pritzker and Jungkunz, Z. Unters. Lebensm. 1927, **54**, 233 ; Kaufmann, Arch. Pharm. 1925, **263**, 675 ; Heiduschka and Wiesemann, J. pr. Chem. 1930 [ii], **124**, **240** : the figure of 10% recorded for an authentic almond oil by Bertram, Z. deut. Oel- u. Fett-Ind. 1925, **45**, 733, must be regarded as exceptional), 80–84% of oleic acid and 15–20% of linolic acid. Almond oil is used chiefly for pharmaceutical and cosmetic preparations. Owing to its high price it is liable to adulteration with other oils from the *Prunus* family—chiefly with apricot-kernel and peach-kernel oils, which closely resemble almond oil, but have a less pleasant taste. These two oils, from the kernels of *P. armeniaca* (Linn.) and *P. persica* (Batsch) (=*P. persica*, (Stokes)) respectively, constitute the *Oleum Persici*[2] of the British Pharmaceutical Codex, and can replace almond oil for a number of its applications.

Apricot and peach-kernel oils have slightly higher iodine values (96–108) than almond oil, but their detection in admixture with the latter is a matter of considerable difficulty. Tests depending on the development of a characteristic red colour when samples containing apricot-kernel oil are shaken with (*a*) nitric acid (sp.gr. 1·4)[3], or (*b*) one-fifth volume of a mixture of equal parts of concentrated sulphuric acid, fuming nitric acid, and water (*Bieber's reagent* : Bieber, Z. anal. Chem. 1878, **17**, 264, *cf.* Ross and Race, Analyst, 1911, **36**, 263)[4] or (*c*) two volumes of a mixture of equal parts of nitric acid (sp.gr. 1·45) and a 0·1% solution of phloroglucinol in ether (*Kreis reagent: cf.* Kreis, Chem.-Ztg. 1902, **26**, 897 ; Chwolles, *ibid.* 1903, **27**, 33; Lewkowitsch, Analyst, 1904, **29**, 109, 110) are valuable as confirmatory tests, but must not be regarded as infallible. In the case of rancid oils, the tests may fail ; also, although almond oils usually do not change colour in these tests, cases have been recorded of authentic fresh specimens which showed faint pink colorations (*cf.* Lewkowitsch, Chem. Tech. of Oils, Fats, and Waxes, 6th Ed., vol. II, p. 300 ; Pritzker and Jungkunz, Z. Unters. Lebensm. 1929, **57**, 85 ; Heiduschka and Wiesemann, *l.c.*). Negative results or faint pink colorations may be obtained with authentic peach-kernel oils, while cherry-kernel and plum-kernel oils also give orange or reddish colorations in the Bieber test. E. L.

ALMOND OIL, ESSENTIAL (*v.* OILS, ESSENTIAL). This is obtained by distillation with water from the marc left after expression of the fixed oil from the seeds of bitter almonds, *Prunus amygdalus*, var. *amara*, N.O. Rosaceæ. The oil results from the hydrolytic action of a nitrogenous ferment, *emulsin*, found in both sweet and bitter almonds, on the glucoside amygdalin which exists only in the bitter almond, yielding benzaldehyde, glucose and hydrocyanic acid :

$$C_{20}H_{27}NO_{11}+2H_2O$$
$$=C_6H_5{\cdot}CHO+HCN+2C_6H_{12}O_6$$

---

[1] *Ol. Amygdal. Exot.* refers to genuine almond oil, expressed abroad and complying with the requirements of the French Codex.

[2] The bulk of the commercial peach-kernel oil or *persic oil* is in fact derived from apricot kernels, but the term is also used as a more or less generic title to cover the non-official grades of almond oil.

[3] Mohler and Benz (Z. anal. Chem. 1933, **94**, 184).

[4] Harry (Pharm. J. 1936, **136**, 199).

The reaction occurs in three stages, as almond emulsin is a mixture of three enzymes which act consecutively, (1) *amygdalase* yields glucose and an amygdonitrile glucoside (*prunasin*), (2) *β-glucase* yields β-glucose and *d*-mandelonitrile, and (3) *cyanase* yields benzaldehyde and hydrogen cyanide.

The yield of essential oil varies according to the quality of the almonds and according to the proportion of sweet almonds mixed with the bitter. The marc yields on an average 1% of oil corresponding to about 0·5% from the original almonds. Characters : sp.gr. 1·045–1·070 ; optically inactive, n_D^{20} 1·543–1·544. It contains 90–95% benzaldehyde, 4–6% hydrocyanic acid and benzalcyanhydrin,

$$C_6H_5{\cdot}CH(OH)CN$$

It is purified by redistillation with lime and ferrous sulphate, or by agitation with a saturated solution of sodium bisulphite and distilling the crystalline bisulphite compound of the benzaldehyde with caustic soda. The purified oil known in commerce as almond oil S.A.P. (sine acid prussic) has sp.gr. 1·048–1·052, optically inactive, n_D^{20} 1·540–1·545. It is used as a flavouring agent for emulsions and for culinary purposes.

Essential oil of almonds is very rapidly oxidised on exposure to moist air, forming benzoic acid, but when carefully dried by immersing in it a piece of fused calcium chloride it is said to keep indefinitely. It may be adulterated with synthetic benzaldehyde or with alcohol. The former, if free from chlorine compounds, is impossible of detection; the latter is detected by shaking with water and applying the iodoform test to the washings.

An oil similar in character is obtained from peach and apricot kernels. C. T. B.

ALOCOL. Trade name for colloidal aluminium hydroxide, which is used as a remedy for hyperacidity.

ALOE-EMODIN. β-Hydroxymethyl-1 : 8-dihydroxy anthraquinone, m.p. about 218°, contained in aloes, rhubarb, and senna leaf. Purgative.

ALOE FIBRES. Fibres of Agave species (*q.v.*) (Fam. Amaryllideæ) which include sisal hemp, are sometimes termed aloe fibre, vegetable silk, or "pita" (G. Watt, "Commercial Products of India," 1908, 35). Of the same family is Mauritius hemp or aloe fibre from *Fourcroya fœtida*. Fibres of genuine aloe species (Fam. Liliaceæ) are less important, *e.g.* those of *Aloe lugardiana* of Bechuanaland used for ropes. Confusion has been caused because the popular name for the cultivated agave is aloe.

ALOE RESINS *v.* ALOES OR BITTER ALOES.

ALOES or BITTER ALOES (*Aloès*, Fr. ; *Aloe*, Ger. ; *Aloe*, B.P., U.S.P.) is the more or less inspissated juice of the succulent leaves of various species of *Aloe* (N.O. Liliaceæ). Slow concentration, followed by partial crystallisation of the aloin, yields an opaque *livery* or *hepatic* variety ; rapid and more complete concentration yields a drug that breaks with a vitreous fracture into translucent homogeneous splinters, and is termed *vitreous*, *lucid*, or *glassy*, and shows no crystals under the microscope. According to the geographical source three main varieties are distinguished, all of which may be either hepatic or lucid.

1. *Curaçao* (*Barbados*) *Aloes* (from *A. vera* L. or possibly from *A. chinensis* Baker), now produced almost exclusively in the Dutch West Indian islands, and scarcely any longer in Barbados. The better varieties are opaque, yellowish brown to chocolate brown, and form the chief source of aloin.

2. *Cape Aloes* (from *A. ferox* Miller), dark reddish brown or nearly black and vitreous, is the chief variety used in Germany ; in Britain mostly for veterinary purposes.

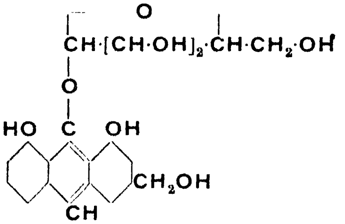
3. *Socotrine Aloes* (from *A. Perryi*, Baker), from the island of Socotra and the east coast of Africa, is usually imported in a pasty or semi-liquid condition and has an unpleasant odour On further drying it forms dark brown *livery* masses. Zanzibar aloes is a variety often closely resembling that from Curaçao.

Reactions.—Pure aloes is soluble in ether and almost completely so in water ; the aqueous solution is coloured dark brown by alkalis and black by ferric chloride. With concentrated nitric acid Curaçao aloes becomes at once deep red, Socotrine and Zanzibar aloes become reddish brown, Cape aloes gradually green. All these varieties show a green fluorescence in aqueous solution (1%) when powdered borax (5%) is added. This reaction, due to barbaloin, is not given by the obsolete Natal aloes, which contain nataloin. All varieties (except that from Natal) give Borntraeger's reaction for aloe-emodin : dissolve 0·1 grm. in boiling water, cool, shake with 10 c.c. benzene, separate the benzene layer and shake it with ammonia, which is coloured red. Curaçao aloes is the only variety containing appreciable quantities of *iso*barbaloin, and alone gives typically Klunge's reaction for this substance : to 10 c.c. of a freshly prepared 0·1% aqueous solution of aloes add 1 drop of a 5% copper sulphate solution, a trace of sodium chloride, and a few drops of alcohol ; a fine wine-red colour is produced (Ber. 1883, **16**, 691). Aschan (Arch. Pharm. 1903, **241**, 340) has tabulated the reactions of the chief varieties.

Constituents, Analysis, Detection.—Apart from barbaloin, aloes contains amorphous water-soluble constituents, resins, a little aloe-emodin (a constituent of rhubarb, *q.v.* ; *see also* Tutin and Naunton, Pharm. J. 1914 [iv], **37**, 836), and ash 1·5–3% ; less than 4%, U.S.P. For analysis, *see* Tschirch and Hoffbauer, Arch. Pharm. 1905, **243**, 399 ; van Itallie (Pharm. Weekblad, 1905, **42**, 553 ; Seel, Arch. Pharm. 1919, **257**, 212, 229, 254). For recognition (*post mortem*) and in urine, *see* Hall and Keightley, Analyst, 1933, **58**, 518 ; 1934, **59**, 152.

Aloin (B.P., U.S.P.) is a crystalline yellow powder, consisting of barbaloin and the isomeric *iso*barbaloin ; the amount in Curaçao aloes (the chief source) is 10–30% ; African varieties contain less (Cape 5–9%) and a much larger amount of amorphous β-barbaloin, formed from barbaloin by heating to 160° and evaporation of the juice at a high temperature. It is used in medicine as a purgative (0·1–0·3 grm.), is the basis of most "patent" pills, and is used as a hop substitute. Various means have been proposed for converting aloin into (insoluble and) tasteless compounds, *e.g.* by condensation with formaldehyde.

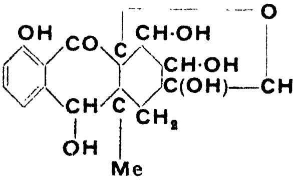
Barbaloin is prepared by extracting aloes with two parts of water at 90°–95°; the crystals which separate after some days, when recrystallised several times from alcohol, are small, yellow, prismatic needles containing water of crystallisation, and when anhydrous melt somewhat indefinitely at 145°–150°. $[\alpha]_D$ −10·4° in ethyl acetate (Léger), −8·3° in 90% alcohol (Jowett and Potter, J. Chem. Soc. 1905, **87**, 878). There has been considerable controversy about its molecular formula and constitution. It is certain that when boiled with borax the solution yields aloe-emodin and anthranol (Hauser, Pharm. Acta Helv. 1931, **6**, 79; McDonnell and Gardner, J. Amer. Chem. Soc. 1934, **56**, 1246). Previously Léger (Compt. rend. 1902, **134**, 1111, 1584; 1910, **150**, 983, 1695; 1912, **155**, 172) had shown that alcoholic hydrogen chloride produces *d*-arabinose and aloe-emodin (a secondary oxidation product of the above anthranol). Hence Rosenthaler (Arch. Pharm. 1932, **270**, 214) assigned the following constitution to barbaloin:



On this view it is a 9-*d*-arabinoside of 1 : 8 : 9-trihydroxy-3-hydroxymethylanthracene. (The isomeric formula, with the arabinose group in 10, is less likely.) Léger's views had already demanded a change of the old empirical formula for barbaloin $C_{16}H_{18}O_7$ to $C_{20}H_{18}O_9$ and Rosenthaler considers the substance to be $C_{20}H_{20}O_8,1\frac{1}{2}H_2O$. The higher molecular weight was confirmed through molecular weight determinations by Seel and Kelber (Ber. 1916, **49**, 2364) and by the analysis of halogen derivatives by Gibson and Simonsen (J. Chem. Soc. 1930, 553), but later Cahn and Simonsen (*ibid.* 1932, 2573) reverted to the old formula

$$C_{16}H_{18}O_7$$

and suggested the constitution



On this view barbaloin is not a glucoside and only a potential anthracene derivative. The action of borax would not be a simple hydrolysis and according to Cahn and Simonsen does not yield *d*-arabinose; they consider that it is only produced in small yield under abnormal conditions by a side reaction in Léger's degradation. They represent the formation of the anthranol by the equation:

$$C_{16}H_{18}O_7 \rightarrow C_{15}H_{12}O_4 + MeOH + H_2O + O$$

and state that the yield of the anthranol, formed by intermolecular dismutation in the presence of borax, is poor, unless hydrazine is added as oxygen acceptor. They attach little weight to molecular weight determinations and base the formula $C_{18}H_{18}O_7$ largely on analyses of their *barbaloin pentamethylether*, crystals, m.p. 177°–179°, $[\alpha]_{5461}$ −12·05° in chloroform. At present no verdict seems possible in this remarkable controversy, although a C_{20} formula seems more likely, when the above substance of Cahn and Simonsen would be a heptamethyl ether.

iso*Barbaloin* occurs in Barbados aloes to the extent of 0·5% and yields, according to Léger, the same hydrolytic products as barbaloin (Compt. rend. 1910, **150**, 1695).

Nataloin, m.p. 203°, occurs in Natal aloes (14%) and, according to Léger (J. Pharm. Chim. 1903 [vii], **17**, 13), yields by hydrolysis arabinose and by oxidation natalo-emodin methyl ether, the ether of a trihydroxyanthraquinone. Nataloin does not give Klunge's or Borntraeger's reaction, and with nitric acid does not yield chrysammic acid,

$$C_{14}H_2O_2(OH)_2(NO_2)_4,$$

but merely picric and oxalic acids. G. B.

ALOES WOOD. A name applied to the wood of *Aquillaria Agallocha* (Roxb.), a leguminous tree of Cochin China, and to that of *A. malaccensis* (Lam.) of tropical Asia. Both are highly fragrant and aromatic; used in fumigations and pastilles, and occasionally by cabinet-makers and inlayers.

An essential oil obtained from *Bursera delpechiana* is known as Mexican Linaloe oil (*v.* OILS, ESSENTIAL). C. T. B.

ALOINOSE *v.* ARABINOSE.

ALOINS are compounds of pentoses and hydroxyanthraquinone derivatives in which it is believed a phenolic hydroxyl is attached to the terminal hydroxyl of the sugar, the aldehyde group being free. The best known is Barbaloin.
E. F. A.

ALOXITE. Registered trade name of the Carborundum Company for its fused alumina.

ALPACA is a long silky fibre derived from the fleece of a South American mammal, *Lama huanaco*, var. *paco*, which grazes at 14,000 to 16,000 feet above sea-level. Alpaca cloth is now usually made from mohair or wool.

ALPAX. A light alloy of silicon (13% Si) and aluminium, *v.* ALUMINIUM and ALLOYS, LIGHT.

ALPHANOL-BLACK, -BLUE, -FAST GREY, -YELLOW-BROWN are acid azo-dyestuffs.

ALPHOGEN, ALPHOZONE. Trade names for succinyl peroxide.

ALPHOL. α-Naphthyl salicylate,

$$C_6H_4(OH)CO_2C_{10}H_7.$$

Antiseptic.

ALPINIA OFFICINARUM *v.* GALANGA ROOT.

ALPINIA OIL. An essential oil obtained from the leaves of *Alpinia malaccensis* ; sp.gr. 1·02 at 26°, optical rotation +6·5°. Consists mainly of methyl cinnamate, together with *d*-pinene (Van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1900, **3**, 451). C. T. B.

ALPININ *v.* GALANGA-ROOT.

ALQUIFON, Black lead ore or Potters' ore. A native lead sulphide, used by potters to glaze coarse ware.

ALSACE GREENS. Nitroso-dyestuffs, *e.g.* dinitrosoresorcinol.

ALSOL. Trade name for aluminium acetotartrate. Astringent and antiseptic.

ALSTONIA BARKS. The barks of various species of *Alstonia* (N.O. Apocynaceæ) contain alkaloids : the best known is that of *A scholaris* (R. Br.) (=*Echites scholaris* L.), a large tree growing in the Indian Peninsula, the Philippines (where it is called Dita), Java, etc. ; it has long been used by native practitioners for various medicinal purposes, particularly against malaria. It was examined by Hesse (Annalen, 1875, **176**, 326 ; Yobst and Hesse, *ibid.* 1875, **178**, 49 ; Hesse, *ibid.* 1880, **203**, 144 ; Ber. 1880, **13**, 1841), who isolated two alkaloids, a weak amorphous base *ditamine*, $C_{16}H_{19}O_2N$, liberated from its salts by ammonia, and a much stronger crystalline base *echitamine*, $C_{22}H_{28}O_4N_2$, only liberated by alkaline hydroxides. The amount of echitamine in Indian bark is about 0·1%, in Dita bark from the Philippines 0·2–0·3% ; Hesse isolated 0·04% of ditamine. Echitamine is identical with "ditaine" of Harnack (Arch. exp. Path. Pharm. 1877, **7**, 126 ; Ber. 1878, **11**, 2004 ; 1880, **13**, 1648). Hesse's results were largely confirmed by Bacon (Philippine J. Sci. 1906, **1**, 1007). Echitamine was also isolated from the bark of *A. spectabilis* R. Br. (0·8%) by Hesse (Annalen, 1880, **203**, 170), from that of *A. congensis* Engl. by Goodson and Henry (J.C.S. 1925, 1640). Goodson (*ibid.* 1932, 2626) gives a table of the total alkaloidal and echitamine content of a number of other *Alstonia* barks, some of which contain no echitamine at all. Echitamine is not well characterised as free base ; Hesse considered that it forms a crystalline hydrate with $4H_2O$. The *hydrochloride*, rapidly crystallised from water, forms anhydrous needles, m.p. 295°, $[a]_D^{15°}-58°$ in water ; on slow crystallisation prisms $C_{22}H_{28}O_4N_2,HCl,H_2O$. For details of other salts, *see* Goodson and Henry and Goodson (*l.c.*).

Echitamine contains one **MeO** and one **NMe** group ; the former is attached to a carbonyl group and on heating the hydrochloride with dilute sodium hydroxide, or even on attempting to crystallise the free base from aqueous alcohol, hydrolysis occurs with the formation of a weaker base $C_{20}H_{25}O_2N{\cdot}COOH$. Goodson and Henry further obtained a diacetyl derivative, which suggests the presence of two hydroxyl groups, and, on distillation with alkalis, monomethylamine and an indole derivative are obtained. Thus echitamine shows considerable resemblances to the alkaloids of *Aspidosperma Quebracho*, being like quebrachine (=yohimbine, *q.v.*) a methyl ester and also an alcohol. Like quebrachamine, but unlike quebrachine, it gives the glyoxylic reaction for tryptophane.

Echitamidine, $C_{20}H_{26}O_3N_2$, was obtained in minute amount by Goodson from the mother-liquor of echitamine hydrochloride of the barks of *A. scholaris* and *A. congensis*. It forms six-sided plates from moist ether, m.p. 135°, $[a]_D$ −515°, and probably lacks the carbomethoxy group of echitamine.

The bark of the Australian *A. constricta* F. Muell. contains quite distinct alkaloids (0·4%). Hesse (Annalen, 1865, Suppl. IV, 40 ; 1880, **205**, 360 ; Ber. 1878, **11**, 1546) obtained amorphous *alstonine* (=chlorogenine) and *porphyrine*, together with crystalline *alstonidine*. This bark was recently examined by Sharp (J.C.S. 1934, 287), who obtained Hesse's alstonine as crystals, together with three amorphous alkaloids. Alstonine forms a yellow micro-crystalline tetrahydrate and fine canary-yellow crystals, $C_{21}H_{20}O_3N_2,1\frac{1}{4}H_2O$, sintering at 87°, resolidifying, and then melting sharply at 254°. The alkaloid is very unstable and is best characterised as the picrate, orange needles, m.p. 194°, and the sulphate, $B_2,H_2SO_4,5H_2O$, m.p. 209°, $[a]_D$ +118·6°. The yield of the sulphate may be 1·3% of the bark. The salts of alstonine form yellow or orange solutions in water with a strong blue fluorescence on dilution. Alstonine contains one **OMe** group but no **NMe**, and does not react with acetic anhydride, benzoyl chloride, or nitrous acid. It gives no reactions for indole nor for methylene dioxy groups.

A number of other Australian species, including *A. villosa* Blum, contain something like 1% of total alkaloids, of which several are crystalline (Sharp, J.C.S. 1934, 1227). The most important is *villalstonine*, $C_{40}H_{50}O_4N_4$, best characterised as the oxalate, $B,C_2H_2O_4$, m.p. 235°, $[a]_D$ +32°. Only two of the nitrogens are basic ; there is one methoxy (probably carbomethoxy) group and there are two **NMe** groups Villalstonine and several other crystalline alkaloids in these barks seem undoubtedly to be composed of two tryptophane residues, like calycanthine, and reminiscent of the "double" *iso*quinoline alkaloids bebeerine, curine, oxyacanthine, *iso*chondodendrine.

No alstonia bark has as yet yielded any alkaloid suitable for the treatment of malaria. G. B.

ALSTONIDINE *v.* ALSTONIA BARKS.

ALSTONINE, *Alstonidine* *v.* ALSTONIA BARKS.

ALSTONITE. A rare mineral consisting of barium and calcium carbonate $(Ba,Ca)CO_3$, crystallising in the orthorhombic system. The small crystals have the form of acute six-sided pyramids, and consist of complex twin intergrowths. Found, associated with witherite, in 1834 in a lead and zinc mine near Alston in Cumberland, and at Fallowfield in Northumberland ; and in 1909 in a coal-mine near Durham. This species is often, but incorrectly, called bromlite (*cf.* BARYTOCALCITE). L. J. S.

ALTAI, *Kronelyne*, T.P.P. Trade name for triphenyl phosphate $(C_6H_5O)_3PO$.

ALTHÆA OFFICINALIS (Fam. Malvaceæ), Marsh Mallow. The root contains

25–35% of mucilage (glucosan and xylan), a fatty oil consisting of the glycerides of palmitic, oleic, and butyric acids, and a phytosterol. The extract is used as an emollient.

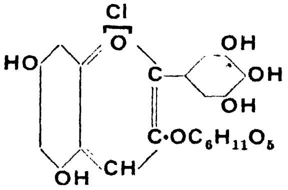
ALTHÆA ROSEA. Hollyhock. The seeds contain a solid yellow fat, iodine number 84·8, n_D^{40} 1·4691 (J. Pierarts, Les matières grasses, 1927, **19**, 7779).

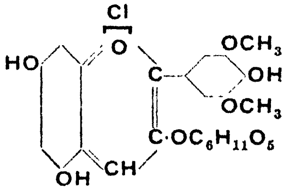
ALTHEIN (*v.* PLANT PIGMENTS), the pigment of the black hollyhock (*Althæa rosea* (Cav.)), has been isolated and described by Willstätter and Martin (Annalen, 1915, **408**, 110 ; *cf.* Polyt. Zentralblt. 1860, 1540 ; Glan, Dissertation Erlangen, 1892 ; Grafe, Sitzungsber. Akad. Wiss. Wien, 1911, 765). The *chloride*,

$$C_{22}H_{23}O_{12}Cl,$$

which crystallises in brown-red prisms containing $4H_2O$, is easily soluble in water, dilute HCl, dilute H_2SO_4 or in methyl or ethyl alcohol, but almost insoluble in glacial acetic acid ; it gives with ferric chloride a violet-blue colour in alcohol, and violet in water ; sodium carbonate produces a blue colour when added to an acid solution. It is optically active, $[\alpha]_{623}-655°$; $[\alpha]_c-545°$; $[\alpha]_{692}-291°$ (W. and M., *l.c.*). The *picrate* is crystalline and difficultly soluble.

It has been shown by Karrer and Widmer (Helv. Chim. Acta, 1927, **10**, 12) that althein is a mixture of the monoglucosides of delphinidin and of its dimethylated derivative malvidin. They separated the two anthocyanins by fractional crystallisation of their picrates.





R. S.-M.

ALTROSE, $C_6H_{12}O_6$, is a stereoisomeride of glucose ; *d*- and *l*-altrose have been obtained synthetically from the corresponding riboses together with *d*- and *l*-allose, *q.v.*

E. F. A.

ALUDEL. The aludels of the earlier chemists were pear-shaped pots generally made of earthenware, but sometimes of glass, open at both ends. Each aludel had a short neck at the top and bottom, so that a series of them could be fitted together by means of the necks. The earthenware pear-shaped vessels in which the mercurial vapours are condensed at Almaden in Spain are also known as aludels.

ALUM *v.* ALUMINIUM.

ALUMATOL. This explosive, which has been used for charging trench mortar bombs, etc., consisted of ammonium nitrate 77%, trinitrotoluene 20%, and aluminium powder (flake), 3%.

H. S.

ALUMINATES *v.* ALUMINIUM.

ALUMINIUM.

Occurrence.—The earth contains about 15% of alumina, or 7 to 8% of aluminium. It is the most prevalent metal on the earth's crust and the third element in order of abundance, oxygen leading with 50% and silicon coming next with 25%. It does not occur in the elemental form in nature.

The principal minerals used as sources of the metal are bauxite and cryolite. Included in the aluminium minerals are the following. Oxides : *Corundum* Al_2O_3, or, coloured by metallic oxides, *ruby* and *sapphire*. Hydroxides : *Diaspore* $Al_2O_3{\cdot}H_2O$, *Bauxite* $Al_2O_3{\cdot}2H_2O$, *Hydrargillite* $Al_2O_3{\cdot}3H_2O$. Aluminates : *Spinel* $Mg(AlO_2)_2$, *Iron spinel* $Fe(AlO_2)_2$, *Chrysoberyl* $Be(AlO_2)_2$, *Zinc spinel* $Zn(AlO_2)_2$, and complexes such as *Chrome spinel* $(Mg,Fe)(Al,Fe,Cr)_2O_4$. Fluorides : *Cryolite* $3NaF{\cdot}AlF_3$, *Chiolite* $5NaF{\cdot}AlF_3$, *Fluellite* AlF_3,H_2O, and complex fluorides as *Parchuolite* $AlF_3{\cdot}NaF{\cdot}CaF_2,H_2O$. Sulphates : *Alum* $(NH_4,K,Na)Al(SO_4)_2,12H_2O$, *Kalinite* $KAl(SO_4)_2,12H_2O$, *Alunite*,

$$K(H_2AlO_2)_3(SO_4)_2,3H_2O,$$

Aluminite $(AlO)_2SO_4,9H_2O$, and many complex sulphates which may contain Mn, Zn, Mg, Cu, Fe, Ca, Ni and Co. Carbonates : *Dawsonite* $NaAl(OH)_2CO_3$, *Mellite*,

$$Al_2C_{12}O_{12},18H_2O.$$

Phosphates : *Turquoise* $Al_2(OH)_3PO_4,H_2O$, *Wavellite* $(AlOH)_3PO_4,4\frac{1}{2}H_2O$, *Callaite* $AlPO_4,2H_2O$, and complex phosphates containing Mg, Fe, Ca, Mn, Cu, Pb, Na. Arsenates : *Durangite* $Na(AlF)AsO_4$, *Synadelphite*, $Mn_5Al_2(OH)_{10}(AsO_4)_2$, and other arsenates containing Fe or Cu. Borates : *Jeremejeffite* $AlBO_3$ and *Rhodizite* $KAl_2B_3O_8$. Silicates : *Cyanite*, *Andalousite*, or *Sillimanite* $SiO_2{\cdot}Al_2O_3$, *Kaolinite* $Al_2O_3{\cdot}2SiO_2,2H_2O$, *Kochite* $2Al_2O_3{\cdot}3SiO_2,5H_2O$, *Feldspars*, *Orthoclase* $KAlSi_3O_8$, *Albite* $NaAlSi_3O_8$, *Anorthite* $Al_2Ca(SiO_4)_2$, *Leucite* $KAl(SiO_3)_2$, *Nephelite* $(KNa)AlSiO_4$, *Spodumene* $Li{\cdot}Al(SiO_3)_2$ *Beryl* $Be_3Al_2Si_6O{\cdot}_8$, *Zeolites*, hydrated silicates of aluminium and an alkali metal or calcium. Complex silicates : *Topaz* $Al_2F_2SiO_4$, *Tourmaline*, borosilicate of aluminium containing alkalis, iron, magnesium, fluorine, and water, *Lazurite*, silicate of aluminium containing some sulphur and chlorine ; *Axinite* $Al_2Ca_3HBSi_4O_{16}$, *Sodalite* $Al_3Na_4Cl(SiO_4)_3$. Small amounts of alumina have been found in natural waters and in the ashes of plants, meat, and milk.

History.—Oersted in 1824 prepared aluminium by reducing aluminium chloride by means of potassium amalgam and distilling the mercury from the metallic residue. In 1845 Wöhler obtained small spheres of metal by reduction of the chloride with potassium. In 1854 H. St. C. Deville obtained aluminium in quantity by reducing aluminium sodium chloride with sodium. About this time both Deville and Bunsen produced small amounts of aluminium by the electrolysis of fused aluminium sodium chloride. E. and A. Cowles in 1886 produced alloys of aluminium, particularly aluminium bronzes, by the reduction of alumina in presence of copper by means of carbon in an electrically heated furnace. Pure aluminium cannot be obtained satisfactorily by this process as it remains, to a great extent, mingled with the carbon unless there is some other metal present, such as copper, which collects the aluminium vapour forming an alloy.

The electrolytic process.—The sodium aluminium chloride used by Bunsen and by Deville was unsatisfactory, as it could not be used, owing to volatilisation, at sufficiently high temperatures for the aluminium to be collected in the molten state. Working below the melting-point the aluminium could not be obtained in a compact mass but tended to form a metal fog.

In 1869 Gaudin selected cryolite as the source of the metal and hoped to keep it molten in a vessel by means of external heat.

In 1882 Lontin used a molten mixture of alumina, cryolite, and other fluorides.

These attempts came to grief over the problem of a material for the crucible: anything of a siliceous nature is dissolved by the molten cryolite and also attacked by the molten aluminium, metal crucibles are attacked by molten aluminium, and carbon crucibles were found to be unsatisfactory owing to porosity.

In 1883 C. S. Bradley patented the use of the current supplied for electrolysis to maintain the heat of the bath by internal resistance heating.

In 1886 Hall in America and Héroult in France patented closely similar processes using the present form of cell, and the practical commercial production of aluminium by electrolysis of cryolite and other fluorides may be said to have begun at this time.

The aluminium produced by the sodium process was very impure, as shown by the following analyses taken from Hoffmann's Ber. Entwick. Chem. Ind. (1), 603.

	1	2	3	4	5	6	7	8	9	10
Locality . .	Paris	Paris	Berlin	Paris	Paris	Paris	Bonn	Nanterre (Morin)		
Analyst . .	Salvétat	Salvétat	Mallet	—	Dumas	Dumas	Kraut	Kraut	Kraut	Sauerwein
Aluminium .	88·35	92·97	96·25	92·60	92·5	96·16	94·7	—	—	97·2
Silicon . .	2·87	2·15	0·45	0·45	0·7	0·47	3·7	0·04	0·12	0·25
Iron . .	2·40	4·88	3·29	7·55	6·8	3·37	1·6	1·62	2·26	2·40
Copper . .	6·38	—	—	—	—	—	—	—	—	—
Lead . .	trace	—	—	—	—	—	—	—	—	trace
Sodium . .	—	trace	trace	—	—	—	—	—	—	—

It is only since the introduction of electrolytic refining process, described later, that aluminium of high purity (99·95% Al or better) has been obtained in commercial quantities.

The Development of the Aluminium Industry.—The first factory established on electrolytic lines was that started in 1888 at New Kensington by the Pittsburg Company, which is now known as the Aluminium Company of America and which operates reduction works at Niagara Falls; Massena, N.Y.; Alcoa, Tenn.; Badin, N. Carolina; Shawinigan, Quebec; and Arvida, Quebec; and alumina works at East St. Louis, Ill.

Other companies operating on a large scale are:

(1) The British Aluminium Company. Reduction works at Kinlochleven, Argyll; Foyers and Lochaber, Inverness-shire; Vigelands and Stangfjord, Norway. Alumina works at Larne Harbour, Northern Ireland; Burntisland, Scotland. Rolling mills at Warrington, and at Milton, Staffs.

(2) Aluminium Français, Paris. Reduction works at La Praz, Calypso, and St. Jean de Maurienne, Savoy; Chedde and Venthon, Haute Savoy; L'Argentière-la-Bassée, Hautes Alpes; Auzat, Ariège; Beyrède, Hautes Pyrénées; Riouperoux and Les Clavaux, Isère; St. Michel de Maurienne; St. Auban, Basses Alpes; Sabananigo, Spain. Alumina works: St. Auban; Salindres, Gard; Gardanne, La Barasse, and St. Louis les Aygaylades, Bouches du Rhône.

(3) Aluminium Industrie Ges. Neuhausen a. Rhein. Reduction works at Bitterfeld; Rheinfelden, Baden; Lend Gastein (Austria). Alumina works at Duisburg; Breslau; Bergheim, Rheinland; and Ludwigshafen.

(4) Vereinigte Aluminiumwerke, Berlin. Reduction works at Lauta, Lausitz; Töging (Innwerk), Oberbayern; Grevenbroich (Erftwerk), Niederrhein. Alumina works: Lautawerk.

Some recent figures for aluminium production are given on p. 266.

Alumina Production.—The raw material best suited to the economic production of alumina is bauxite, of which widely distributed deposits are found in southern France in the Bouches du Rhône, Var, Ariège, and Herault districts; in the U.S.A. mainly in Arkansas, but also in Georgia, Tennessee, and Alabama; in British Guiana and in numerous other localities. The output of Bauxite from various countries is given on p. 266.

The ore "bauxite" varies widely in composition, but for alumina production by the Bayer process it is generally accepted that the alumina content should be at least 55% and the

ESTIMATED WORLD'S PRODUCTION OF ALUMINIUM.

(In metric tons)

Year.	Austria (*a*)	Canada (*a*)	France (*b*)	Germany (*a*)	Great Britain (*a*)	Italy (*b*)	Norway (*b*)	Switz'r-land (*a*)	United States	U.S.S.R	Total
1926	2,700	18,000	23,608	30,000	8,100	1,929	24,429	20,000	68,000	—	194,000
1927	3,000	27,000	25,000	31,700	9,700	2,544	20,847	20,000	72,000	—	210,000
1928	3,000	24,000	25,867	30,500	9,700	3,585	24,779	22,000	95,440	—	239,000
1929	2,700	36,000	29,100	31,500	10,000	7,373	29,142	20.700	102,270	—	270,000
1930	3,500	34,900	24,600	30,200	16,000	7,968	27,357	20,500	104,100	—	269,000
1931	3,000	(*d*) 30,000	18,152	25,000	13,000	11.109	21,420	16,000	80,700	—	219,000
1932	2,000	17,800	14,400	14,100	8,825	13,410	17,787	13,820	47,600	—	152,700
1933	900	16,155	14,300	18,932	10,970	12,070	15,384	7,500	38,700	4,400	141,800
1934	2,100	15,500	15,100	37,158	12,500	12,846	15,346	8,100	33,646	14,400	172,700
1935	2,800	20,556	21,847	70,700	16,033	13,650	15,387	19,432	54,112	25,000	257,000

(*a*) As estimated in previous volumes of "Mineral Industry."
(*b*) Official statistics.
(*d*) Estimated from unofficial data.
(Extract from "Aluminium and Bauxite," by C. L. Mantell.)

WORLD'S PRODUCTION OF BAUXITE.

(In metric tons)

COUNTRY.	1928.	1929.	1930.	1931.	1932.	1933.	1934.	1935.
Austria . . .	(*c*)	(*c*)	5,000	4,000	4,000	3,000	3,000	3,000
British Guiana. .	200,882	220,119	149,345	159,590	84,800	42,000	65,917	116,056
British India . .	14,900	9,200	2,554	Nil.	Nil.	1,100	18	—
Dutch Guiana . .	203,000	219,603	264,556	173,144	126,500	106,372	101,000	120,000
France . . .	636,000	666,300	609,200	403,550	401,400	490,500	528,400	512,800
Germany . .	6,860	6,900	7,000	Nil.	1,640	5,000	6,660	15,000
Hungary . . .	395,974	389,151	31,693	88,136	111,500	72,422	115,000	220,000
Italy (*e*) . . .	162,200	192,774	161,187	67,366	86,600	94,600	131,266	170,000
Jugoslavia . .	49,264	103,366	94,700	62,018	67,100	86,500	84,800	(*b*)190,000
Rumania . . .	650	926	678	381	600	1,200	1,500	—
Spain	181	975	323	Nil.	1,300	2,500	300	—
Ireland . . .	2,320	2,360	2,070	3,395	1,500	700	58	—
United States .	381.454	371,648	335,918	199,039	97,895	156,651	160,371	237,666
Total . . .	2,063,000	2,185,000	1,667,000	1,160,000	975,000	1,063,000	1,198,000	1,600,000

(*b*) Estimated. (*c*) Data not available. (*e*) Istria included under Italy.
(Extract from "Aluminium and Bauxite," by C. L. Mantell.)

silica not more than 3%. Anderson ("Metallurgy of Aluminium and Aluminium Alloys") states that bauxite containing less than 50% Al_2O_3, and up to 7% SiO_2, is used in America for alumina production. Silica reacts with the caustic soda and alumina in the kiers to form an insoluble precipitate $Na_2O{\cdot}Al_2O_3,SiO_2,9H_2O$, thus causing a loss of soda and alumina in the residue. Titanium oxide also causes a loss of some soda due to the formation of an insoluble titanate.

Analyses of various bauxites are given below :

Source.	Al_2O_3.	Fe_2O_3.	H_2O.	SiO_2.	TiO_2.	CaO.
Brignoles, red . . .	60·7	21·38	12·9	1·76	3·21	—
,, white . . .	62·87	3·57	15·08	14·3	4·10	—
Vins, red	64·6	17·95	13·35	0·9	3·05	—
,, white	70·38	4·22	13·90	8·2	3·10	—
Mazangues, red . . .	61·0	21·50	12·10	2·9	2·50	—
,, white . .	70·74	2·01	15·80	8·0	3·40	—
Le Luc, red . . .	60·30	20·27	12·72	2·8	2·96	0·68
Mausanne, white . .	60·2	3·45	19·80	12·3	3·70	—
Paradou, red . . .	57·8	21·30	15·1	2·7	2·90	—
Bedarieux, white . .	78·53	0·67	15·1	1·6	3·70	—
Ariège, pink . . .	64·8	4·71	14·79	12·02	3·32	—
Vogelsberg	50·92	15·71	28·60	1·10	3·2	0·8
Pescina	41·13	24·81	17·31	6·28	2·70	8·24
Ireland	35·0	38·0	21·5	3·5	2·0	—
Gold Coast	60·55	9·75	25·59	1·42	2·21	0·73
India, Bihar . . .	69·0	3·0	15·0	12·0	—	—
,, Bihar . . .	55·6	25·3	11·0	3·0	—	—
,, Katui	65·48	3·77	19·38	0·38	11·61	—
West Australia . . .	44·66	19·08	27·02	5·96	3·10	—
British Guiana (average)	61·0	1·5	31·0	2·75	2·75	—
U.S.A. (range of results)	40 to 62	0·81 to 18	16 to 33	0·7 to 20	0·23 to 3·6	—

The following analyses by Leop. Mayer and O. Wagner (Dingl. poly. J. 1883, **248**, 213) show that the appearance of bauxite cannot be relied on as a criterion of its value. Samples Nos. 1–6 were from Feistritz in the Wochein, No. 7 from Pitten, near Wiener-Neustadt. The latter, though resembling bauxite in physical properties, is in reality clay-ironstone.

	Appearance.	Hygroscopic moisture.	Combined water.	Al_2O_3.	Fe_2O_3.	SiO_2.	MnO_2.	CaO.	MgO.	P_2O_5.
1	Pure white .	2·33	13·86	29·80	3·67	44·76	—	2·75	0·84	1·47
2	Yellow . .	1·03	27·85	43·22	14·39	10·43	—	1·61	—	1·13
3	,, . .	1·30	27·70	50·38	11·68	8·34	trace	trace	trace	0·61
4	Red . . .	1·34	23·12	33·86	25·69	12·41	2·42	trace	—	0·53
5	,, . . .	1·31	23·81	46·18	22·05	4·82	—	0·89	—	0·66
6	,, . . .	0·95	20·83	62·10	6·11	5·06	2·01	3·20	trace	trace
7	,, . . .	1·17	4·75	21·80	3·75	60·10	—	6·06	2·49	trace

For the manufacture of the purest form of alumina the bauxite is first roughly powdered and calcined to get rid of water and any organic matters. It is then more finely ground and introduced gradually with agitation into kiers containing caustic soda solution of 1·45 sp.gr. The kiers are now closed and the charge heated for some hours under high-pressure steam—about 70–80 lb. The contents of the kiers are then transferred to the filter presses, and the filtrate further cleared through wood pulp in lead-lined vats. The liquor contains sodium aluminate $NaAlO_2$, which may be decomposed by a current of carbon dioxide, but it is now more usual to adopt the Bayer method of precipitating the alumina. This method depends on the fact that the addition of alumina effects the decomposition of the aluminate and throws down some 70% of the alumina. The solvent liquor now contains alumina and soda in the proportion $Al_2O_3 : Na_2O :: 1 : 6$. The precipitated hydrate of alumina is allowed to settle, and the liquor with its undecomposed portion is run off into weak-liquor tanks. The hydrate is filter-pressed, sufficient being left in the vat to serve as precipitant for the next charge. The weak liquor may, after concentration, be used again for reacting upon a further amount of bauxite.

The hydrate of alumina so obtained ought to contain less than 0·5% of mineral impurity, iron and silicon being the most objectionable of these. To bring it into a suitable physical condition for use in the reduction furnaces it must be calcined at 1,100° to 1,200°, so that it shows no tendency to give up moisture when used in the furnace or to absorb moisture when exposed to air.

On heating, the alumina undergoes a change in its state of aggregation accompanied by the evolution of some heat, the change being apparently of the nature of a reduction in area by increase in size of the aggregates. The high temperature required to bring about this change can be lowered by the addition of hydrofluoric acid, or aluminium fluoride, to the hydrate (Péchiney, F.P. 349709, 1905). Other fluorides such as fluorspar and cryolite produce the same effect.

The press cake containing the impurities removed in the preliminary treatment of bauxite constitutes usually over 30 % of the ore, whether the wet process of extraction or the dry fusion process with sodium carbonate be used. In the latter case, the residue has been successfully applied in the removal of sulphuretted hydrogen from coal gas, or from exit gases of other products. The residue from the wet process is, however, inactive in this respect, but may be transformed into a condition in which it is very effective.

Other processes for alumina production are based on fusion of bauxite with sodium carbonate; action of strong caustic soda on leucite, clay and other silicates; action of sodium carbonate solution on felspar, dissolving silica and leaving alumina; action of hydrochloric or nitric acid on leucite; or of sulphuric acid on clays, etc.; treatment of alunite in various ways; fusing clay with sodium and calcium carbonates; heating aluminous material with sodium sulphate and carbon; reaction on heating sodium chloride, alumina, and steam; salt, red bauxite, and carbon heated in air, sulphur dioxide and steam; heating aluminium silicate and calcium chloride in presence of steam and air. The extraction of alumina from cryolite and from phosphate ores has also been suggested. In other processes clay is heated with ammonium sulphate or sodium bisulphate, or treated with hydrofluoric acid or fluorides. In the Serpek process aluminium nitride was made by heating alumina, carbon and nitrogen at about 1,800°C., this nitride being subsequently decomposed with steam; the hopes raised at one time by this process have not been realised.

Very many minor variations of the above and other reactions have been tried; a concise account of them occupies 157 pages of "The Aluminium Industry," by Edwards, Frary, and Jeffries.

The following processes may be noted :

Seailles. F.P. 634430 (1927). Calcines bauxite at 500°–700°C. with alkaline earth base and extract with soda.

Rochette. F.P. 519819 (1921). Fuses bauxite, limestone, and anthracite in the electric furnace and extract with soda.

Pedersen. B.P. 232930 (1926). Iron ore, limestone, and bauxite are fused in the electric furnace. Iron is tapped off and the aluminous slag is leached with sodium carbonate and caustic soda. Production of the order of 12,000 tons of alumina per year by this process is carried on in Norway.

Haglund. B.P. 232540 (1925). B.P. 234830 (1925). Canad. P. 282065 (1928). Bauxite is fused with pyrites and anthracite. The mixed slag is crushed and leached, treated by clarifying and concentrating, and the crystalline alumina washed with sulphuric acid.

Berger. Magnesium chloride, clay, pyrites and a small amount of iron filings are heated and aluminium chloride distils over. The chloride is mixed with sodium and potassium chlorides and electrolysed to give aluminium.

Blanc. B.P. 176770 (1922). Leucite is leached with hydrochloric acid and the potassium chloride crystallised out. The aluminium chloride is then decomposed by heat, the hydrochloric acid being regenerated.

Halvorsan. B.P. 120035 (1919). Labradorite is digested with nitric acid and the separated solution is heated in an autoclave at about 200 lb. pressure with ammonium salts. The alumina is precipitated in a powdery form easy to filter and wash.

Hall process, or Aluminium Co. of America's process. Frary, U.S.A.P. 1534031 (1925); also B. T. Horsfield, E.P. 248360, 16/2/23. Bauxite of graded composition is mixed with coal and sintered at about 1,000°C. A further quantity of coke is added and the mixture is smelted in a furnace using Soderberg electrodes. The ferro-silicon and ferro-titanium are tapped off at the bottom of the furnace and the pure alumina blown in the form of fine granules by steam and air from the top of the fluid mass in the furnace. The alumina is then further purified by leaching with sulphuric acid.

The Making of Carbon Electrodes.—Bituminous coal, anthracite, retort carbon, natural or artificial graphites, soot and oil-coke are all materials which have from time to time been used in the production of carbon electrodes. In deciding which of these materials should be used, account must be taken of : (*a*) supply and cost of raw material; (*b*) ash content; (*c*) amount of volatile matter and sulphur; (*d*) conductivity for electricity and heat.

Oil coke and pitch coke are still in use, but, with modern methods of coal cleaning, coal coke is produced of sufficient purity to replace anthracite for electrodes for aluminium production. These electrodes differ in character from those used for lighting or for the production of calcium carbide or for many other purposes where graphitisation of the carbon is an advantage and the presence of mineral matter quite permissible and even necessary. The graphitisation of amorphous carbon, which must contain mineral impurities, is indeed effected by exposing it to a high temperature under electrical heating. It is said that at the temperature employed the iron volatilises. Be this as it may, the ash of such carbon contains a considerable amount of oxide of iron. Aluminium, boron, silicon, and other elements which form carbides can be used as graphitising agents, as also to some extent, the oxides of these elements.

Graphite or graphitised electrodes have at

1,000°C. about 5 times the electrical conductivity of coke blocks and 8 to 10 times the thermal conductivity, but it is now recognised that these properties, advantageous in some respects, are not however favourable to the efficient working of reduction furnaces.

It may be taken that, so far as they are capable of reduction in the aluminium furnace, the mineral ash contained in the carbon and the foreign matter present in the alumina form alloys with the aluminium. The amount of alumina used should be about double that of the aluminium resulting therefrom, and the electrode consumption about one-half of the aluminium, so that an estimate may be made of the impurity as silicon contained in the metal. Assuming the silica in the alumina and in the electrode together as 0·4%, in each case, the amount of silicon in the metal will be very nearly 0·2%.

Similar considerations apply to the iron content of the metal, though this may, by reason of operations, much exceed the amount of iron contributed by the alumina and electrodes.

The electrical resistance (in milliohms per cubic inch) of various types of carbon is given below.

	0°.	1000°.
Amorphous carbon (pressed)	1·63	1·45
Graphite carbon . . .	0·32	0·25
Electrodes for aluminium .	3·00	2·60

These figures are only approximate.

The resistance per cubic centimetre would be 2·54 times these values.

In addition to low resistance to the electrical current, it is desirable that electrodes should be of low conductivity for heat and sufficiently hard and resistant to superficial oxidation; they should also be of low porosity and of as even character as possible throughout their whole mass.

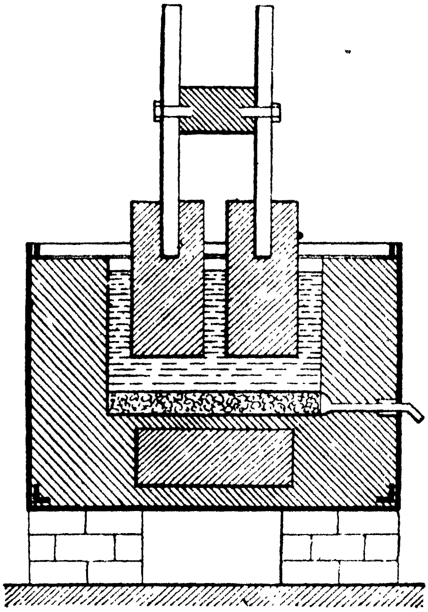
To produce electrodes having these qualities the material (oil coke, pitch coke, anthracite and coal coke, used separately or mixed) must be carefully selected, calcined if necessary, ground, and subjected to high pressure with the admixture of tar and/or pitch to act as binder. The blocks are baked at a temperature of about 1,200° to 1,300° in a kiln, in principle resembling a pottery kiln, the surface of the blocks being protected from oxidation by being embedded in carbon. The permissible current-density for good electrodes of this type when used in the aluminium reduction furnace is in the neighbourhood of 8 amperes per square inch of transverse section.

In addition to text-books on the aluminium industry the following references may be consulted on the subject of electrodes: "The Electric Furnace," Stansfield; pamphlets by the Acheson Graphite Co. and Siemens; "Die künstlichen Kohlen," by Julius Zellner; "Industrial Carbon," by Mantell, Chapman and Hall, London, 1928; Chem. & Met. Eng. 1915, **22**, 23, and R. S. McBride, *ibid.* 1927, **34**, 76. For reference to the Meiser Kiln, *see* Chem. & Met. Eng. 1919, **19**, 179.

With the increase in size of reduction furnaces the size of electrode has been increased and various sizes are now common from 12 in. square by 12 in. high to 16 or 17 in. square. Contact is usually secured by moulding a hole in the end of the anode, before baking, into which an iron foot is placed afterwards, and fixed by pouring cast iron into the space between the iron foot and the block. Soderberg electrodes are at present in use experimentally, the casing, of course, being aluminium, but the use of these continuous electrodes in the aluminium industry offers many difficulties and it is still uncertain whether they will be generally adopted. Compared with an ordinary furnace a Soderberg electrode furnace is extremely expensive, due to the staging required to support the electrode and the raising and lowering gear.

The trend of the aluminium industry has always been toward larger furnaces and with very large furnaces a multiplicity of electrodes of the present type presents some disadvantages which may tell in favour of the Soderberg.

The Reduction Furnaces.—These are iron cases built up of plate and angle iron. The case is usually lined with a layer of some thermal insulator and then lined with carbon mixture rammed into place with pneumatic tools. The diagrammatic figure indicates the general scheme.



The boxes vary in size and shape; in some cases circular cells have been used. The electrodes also vary in size and form, in arrangement in the furnace and in methods of attachment to the anode beam.

Contact with the cathode mixture is usually made by iron bars running through the sides of the furnace. There are relatively few 8,000-

amp. furnaces in use to-day, the present sizes ranging from about 16,000 to 30,000 amp. The increase in size is mainly effective in reducing labour charges, there being little change in chemical efficiency. The distance from the bottom of the anode to the metal remains of the order of 2–4 in. for the large furnaces. With regard to size of furnaces, Billiter gives figures for dimensions of the bath of electrolyte of 180–200 cm. long, 50–75 cm. broad, and 30–40 cm. deep for an 8,000-amp. furnace, and 600–800 cm. long, 70–80 cm. broad, and 50 cm. deep for a 30,000-amp. furnace. Allmand gives 6 ft. by 3 ft. by 6 in. depth for the 14,500-amp. furnaces at Horrem in 1919. It will be seen that there is considerable variation in the relation of the area of the horizontal section of the bath to current rating of cells, but a rough average of about 3·3 amp. to the square inch will work for any size of furnace from 8,000 amp. to 30,000 or over.

J. Billiter ("Technische Elektrochemie," Halle, Saale, 1923–32) mentions that Soderberg electrode furnaces for 40,000 to 50,000 amps. are on trial in America.

In starting a furnace it is usual to introduce first the cryolite, which is brought to a state of fusion by electrical heating. Alumina is then fed in gradually at the surface of the cryolite, and as it dissolves the resistance gradually falls to about 5 or 6 volts, and the temperature of the bath will be generally 1,000°. Starting may be assisted by bringing contributions of molten flux from other furnaces.

When the furnace is running normally the reaction which occurs is mainly equivalent to $2Al_2O_3+3C=4Al+3CO_2$.

There is some CO formed, however, and the gas liberated from the anode is a mixture of the two, but the CO_2 is in the larger proportion except when the "Anode effect" occurs due to shortage of alumina in the bath. When that happens the gas liberated is mainly CO.

Anode Effect.—The running of the furnace is not quite continuous; about two hours after the proper charge of alumina has been added the voltage of the furnace suddenly rises, the flux ceases to wet the anode and the current makes innumerable small arcs from the anode to the flux. This condition indicates that the furnace must be fed with alumina again, when it will run quietly for another two hours or so. The aluminium collects at the bottom of the bath of electrolyte, and is tapped off at stated periods, either every day or at longer intervals.

The flux contains, beside cryolite, more or less sodium fluoride or aluminium fluoride and calcium fluoride according to the working conditions. There is always alumina as well, of course, and the composition is so adjusted by additions, or the setting of working conditions, that the furnace can be worked at about 950°C. or sometimes a little lower.

The melting-point of pure cryolite is 1,005°C., or possibly a little higher (1,023°C., Puschin and Baskow, Z. anorg. Chem. 1913, **81**, 347), that much is certain, but the equilibrium diagram of $NaF–Al_2F_6$ is not so well established, the NaF–cryolite eutectic lying at—

Temp. °C.	Mols. NaF.	Mols. AlF_3.	Reference.
885	86	14	Fedotieff and Iljinsky.[1]
886	86·4	13·6	Lorenz, Jabs, and Eitel.[2]
935	83·5	16·5	Puschin and Baskow.[3]

[1] Z. anorg. Chem. 1913, **80**, 113.
[2] *Ibid.* 1913, **83**, 328.
[3] *Ibid.* 1913, **81**, 347.

Addition of alumina to cryolite produces a mixture of lower melting-point and greater electrical conductivity; this also applies to melts which are not very far away from the composition of cryolite on either the sodium fluoride or aluminium fluoride side. Similar conditions appear when calcium fluoride forms a further constituent of the mixture; in all cases the addition of alumina to a melt, not already containing quantities of it, increases the electrical conductivity at furnace temperatures. At high temperatures, 1,050° or so, addition of alumina decreases the conductivity of cryolite (*see* Parrovano and D'Agostino, Atti R. Accad. Lincei, 1932 [vi], **16**, 186).

The furnace flux is controlled by regular complete analyses, and in different factories by various tests for solubility in water and p_H value of the water extract, also by freezing-point determinations and microscopic examination.

In the analysis of materials rich in aluminium fluoride, Fedotieff and Iljinsky fused the substance with a known weight of sodium fluoride sufficient to bring the mixture to the cryolite composition. This product is attacked by sulphuric acid and the fluorine may be determined by Penfield's method, though the method of Willard and Winter is preferred, in which the material is heated in a distillation flask with perchloric acid, the condensate absorbed in water and titrated with thorium nitrate, using a mixture of zirconium nitrate and alizarin sulphate as an indicator. This method affords a great saving of time and bench space compared with Penfield's process (Chem. News, 1897, **39**, 79).

The purity of all materials is important, as most impurities are reduced and alloyed with the metal in the aluminium furnace.

Metal.—This is removed from the furnace at different works by tapping at a tuyère, by ladling or by pumping. The metal is usually collected in a large ladle and poured into small ingots or into a large settling furnace in which a quantity is accumulated and maintained at a temperature sufficient to allow flux, etc., to separate, after which it is cast into large ingots for rolling, etc. Where metal is cast into ingots without passing through a settling furnace, these ingots are subsequenty re-melted in such a furnace.

According to text-books of petroleum technology, oil coke ash may contain Si, Fe, Cu, Ni, Mn, Ga, Pb, V, Ti, Ag, U, Au, Ca, and Mg. When oil coke anodes are used, it is probable that minute quantities of some or all of these elements will be present in the aluminium. Hartley and Ramage (J.C.S. 1897, **71**, 547) reported traces of Na, K, Ca, Cu, Ag, Mn, Pb, Ga, In; most of these can be found to-day, together with magnesium, carbon, and titanium, sometimes vanadium, nickel, and zinc. Careful tests for arsenic and antimony yield negative results. The main impurities are, of course, iron and silicon, the others, when present, being usually minute traces.

In analysing for traces of alkali or alkaline earth metals it is best to take a large amount of aluminium, even 30 grms. or more, and separate the bulk of the aluminium salts by fractional crystallisation after solution in nitric acid (Fairlie and Brook, J. Inst. Met. 1924, **32**, 283) or hydrochloric acid (Schurmann and Schob, Chem.-Ztg. 1924, **48**, 97).

For the rapid estimation of sodium in aluminium the best process is that of E. Scheuer (Z. Metallk. 1933, **25**, 139) described in his paper on "Der Natriumgehalt des Silumins."

In brief this consists of heating 50 grms. of aluminium in an iron boat in a butt-ended iron tube with the open end loosely plugged with asbestos. The heating is conducted at 900°C. for 20 minutes, whereby the sodium separates and is oxidised. The tube is withdrawn, allowed to cool in the air, and tube, boat, and aluminium are thoroughly washed with water and the washings containing the NaOH titrated with ·01*N*-hydrochloric acid using phenolphthalein as indicator.

Iron determinations are made by titrating the reduced solution of the metal with potassium permanganate, adding ammonium thiocyanate, and titrating back with titanous chloride.

In the case of silicon alloys the metal should be dissolved in the usual mixture of nitric, hydrochloric and sulphuric acids and water. The silica and silicon are then filtered off on to a pad of filter paper pulp, which is washed and ignited. The residue after ignition is fused with alkali carbonates, and the silica then determined as in a clay analysis, after which it is calculated to silicon in the metal.

A small amount of alumina may sometimes be present in aluminium, and from time to time a variety of methods have been suggested for determining it. Most of these methods are worthless, though in the case of granulated aluminium or powder it is possible to get a fairly accurate figure by transformation of the metal into nitrate and calcination of the nitrate to oxide, lightly grinding the oxide and further calcining to a high temperature; the metallic aluminium is calculated from the percentage of impurities in the metal and the weight of oxygen taken up and the difference of the total aluminium, iron and silicon from 100% is taken to be alumina. The best method is that described by Jander and Baur (Z. angew. Chem. 1927, **40**, 486). These investigators volatilise the aluminium as chloride in a stream of HCl gas at about 200°C., about 1 grm. of millings in a porcelain boat being placed in a special tube furnace and the oxygen being removed from the HCl gas by adding about 10% of hydrogen, passing over heated platinised asbestos and careful drying. After volatilisation of the chloride the residue in the boat (containing ferrous chloride and the alumina) is analysed and the alumina determined. In this way the investigators found about 0·1% of alumina in the aluminium they analysed. Their paper also describes the separation of magnesium chloride by porous glass filters from the volatilising aluminium chloride. Other investigations have made use of chlorine gas, but the results are doubtful owing to the difficulty of obtaining pure chlorine and to the action of molten aluminium on the siliceous bond of the boat material, forming silicon and alumina, the reaction between aluminium with chlorine gas occurring at a rather high temperature.

In the case of other elements present in aluminium and its alloys the methods of determination depend primarily on the element and are not peculiar to aluminium.

Aluminium may be obtained from the reduction furnaces with a purity up to 99·8% aluminium, and by electrolytic refining purities of 99·99% Al can be reached. The Hoopes process of electrolytic refining is described by Frary (Trans. Amer. Electrochem. Soc. 1925, **47**, 275). This method employed a cell having three layers of fused material, the bottom (anode) layer aluminium copper alloy, the middle layer cryolite plus barium fluoride, and the top layer (cathode) molten pure aluminium. Since this time processes have been developed using fused mixtures of aluminium chlorides and other chlorides, melting below the melting-point of aluminium. In this case cast slabs of raw aluminium form the anodes, and thin sheets of aluminium form the cathodes (Aluminium-Ind. A.-G., B.P. 265170 of 7/1/27; also B.P. 272246 of 7/6/27; B.P. 280881 of 25/10/27). This very pure aluminium, compared with the usual good metal, has about twice the ductility, half the strength, and a much greater resistance to corrosion.

Recently a process similar to that of Hoopes has been described by R. Gadeau (The Metallurgist, supplement to The Engineer, Dec. 1935). This process is in use at the works of the Compagnie d'Alais, Froges et Camargue. The cell is lined with special magnesia brick having the following composition:

Aluminium fluoride . . .	23%
Sodium fluoride	17%
Barium chloride . . .	60%

As the brick withstands the flux there is no need for a water-cooled section, as in the Hoopes furnace, for insulating the cathode from the anode.

The purest aluminium produced as yet by this process is 99·9986% Al.

Physical Properties.—Aluminium is a white metal capable of taking a high polish and has neither taste nor smell, except that some freshly broken castings have a slight trace of smell reminiscent of the smell of acetylene made from calcium carbide. The metal was described by Deville as crystallising in regular octohedra on slow cooling. The crystal lattice as determined by X-ray investigations is face-centred cubic, the edge of the cube being about 4Å long. The grain size of the crystals in any given piece of aluminium depends on the rate of freezing, the composition, and the mechanical and thermal histories, for example, in an ingot of rolling metal they may be all sizes from less than

1 mm. to about an inch or more. On rolling the crystals are broken up and flattened out until they are no longer recognisable, but on annealing crystal growth occurs. On straining aluminium test-pieces to a certain critical value of the strain practically the whole of the strained area will recrystallise into a single crystal.

The density of molten aluminium is given by Edwards and Moorman (Chem. and Met. Eng. 1921, **24**, 61) as $Dt=2·382-0·000272\ (t-658)$.

The surface tension of molten aluminium has been stated as 520 dynes between 700° and 820°C. (Smith, J. Inst. Metals, 1914, **11**, 168).

The arc spectrum of aluminium shows particularly strong lines at 2652·48, 2660·38, 3082·16, 3092·72, 3944·03, and 3961·54. The lines at 3944·03 and 3961·54 are the last to disappear as the quantity of aluminium is reduced.

The effect of the purity on the electrical conductivity of aluminium is as follows:

Al%.	Conductivity, Cu = 100.
98·5	55
99·0	59
99·5	61
99·6	61·3
99·75	63
99·97	64·6

Tabulated Properties.

Atomic weight	26·97	Int. Atomic Wt. Comm. 1930.
Specific heat at 20°C.	0·214	Bureau of Standards, 1919.
Spec. thermal conductivity, cals. per cm. cube per °C. per sec. at 18°C.	0·504	Lees, Phil. Trans. 1908.
At 100 chill cast	0·51	Griffiths, 1921. Report of Light Alloys Subcommittee.
,, 100 sand cast	0·50	
Melting-point (99·60%)	658·7°	Bureau of Standards, 1915.
,, ,, (99·97%)	659·8°	Edwards, Trans. Amer. Electrochem. Soc. 1925, **47**, 287.
Boiling-point	1800°	Greenwood, Proc. Royal Soc. (1909), **82** [A], 396.
Latent heat of fusion	92·4	Awbery & Griffiths, Proc. Physical Soc. 1926, **38**, 378.
Heat of combustion	380,000	Berthelot, Ann. Chim. Phys. 1878, **15** [v], 242.
,, ,,	380,000	Roth, Z. physikal. Chem. 1928, **144**, 253.
Vapour pressure at m.p., mm. of Hg	0·00062	Millar, Ind. Eng. Chem. 1925, **17**, 34·
At 1,030°C.	1·0	
,, 1,475°	100	
,, 1,800°	760	
Coeff. of linear expansion per °C.	$22·6\times10^{-6}$	Hidnert, U.S. Bureau of Standards paper 497.
Spec. gravity	2·703	B.S.S. No. 215 (1930).
Molten 658·7°C.	2·382	Edwards, "Properties of Pure Aluminium," Trans. Amer. Electrochem. Soc. 1925, **47**, 287.
,, 1,100°	2·262	
Wt. of 1 cu. ft. of aluminium	168·7 lb.	
Electrical resistance at 20°C., microhms per cm. cube for H.D. wire	2·845	B.S.S. No. 215 (1930).
Coeff. of increase of resist. with temp., °C.	0·00407	
Electrochemical equivalent	0·00009316 grms. per coulomb.	
Thermoelectromotive force against platinum Cold junction 0°C.		
Hot junction 100°	+0·412 Mv.	Bureau of Standards, Circ. 346.
200°	+1·06	
300°	+1·88	
400°	+2·84	
Magnetic susceptibility at 18°C.	$0·65\times10^{-6}$	Honda, Ann. Physik, 1910 [iv], **32**, 1027.
	$0·58\times10^{-6}$	Chéveneau, Rev. Gén. elec. 1928, **24**, 7.
Reflectivity for white light	85%	
Solidification shrinkage	6·6%	
Electrode potential in solns. at 25°·1	+1·69 volt	Latimer & Greenfelder, calculated value (J. Amer. Chem. Soc. 1928, **50**, 2202).

Decomposition voltage for aluminium reduction furnace at 1,000°C. . . .	1·7	Edwards, Frary, and Jeffries, "Aluminium Industry," observed value.
	1·38	Thompson and Seyl (Trans. Amer. Electrochem. Soc. 1933, **64**, 321), observed value.
	1·16	Calculated by Thomson and Seyl.
	0·97	Calculated by Newman and Brown (Ind. Eng. Chem. 1930, **22**, No. 9).
Emissivity	0·1113 at 200° 0·153 at 400° 0·192 at 600°	Randolph and Oberholzer (Physical Rev. 1913, **2**, 144).
	0·12 at 700° 0·17 at 1,000°	Moeller and Miething (Giesserei Ztg. 1924, **21**, 444).

The tensile strength of ordinary aluminium is about 6 tons to the square inch, and 99·99% **Al** is about 3 tons to the square inch.

Chemical Properties.—In the course of its production and treatment aluminium takes up gases (chiefly hydrogen and nitrogen), usually in such quantity that their total volume is from 4 to 17% of that of the metal (Hasenbruch, Z. Metallk. 1929, 46). Good metal tapped from the reduction furnaces yields 5 to 10% of its volume of hydrogen and about 3 to 4% of nitrogen. After re-melting, especially under unsuitable conditions, it is found to contain more hydrogen and also carbonic oxide and hydrocarbons; an ingot of metal which had been melted and allowed to cool in the furnace *very* slowly was highly crystalline and found to contain (by volume) the extraordinary amount, viz. 85% hydrogen, 7·5% nitrogen, and 4% carbonic oxide and hydrocarbons. Aluminium is practically unacted upon by oxygen at ordinary temperatures but if finely divided it undergoes considerable oxidation at 400° or even, though less rapidly, at lower temperatures. If sufficiently pure, water has slight action upon it, but this action is accentuated in the presence of copper, brass, or other metals.

The very great affinity which aluminium possesses for oxygen has been made use of in the application of "thermite" as a means of reducing oxides. Goldschmidt (D.R.P. 96317, 1895) has thus used the finely divided metal in the production of iron, manganese, chromium, nickel, cobalt, titanium, boron, molybdenum, tungsten, vanadium and other metals.

Carbon or the oxides of carbon at high temperatures convert aluminium into the carbide, Al_4C_3.

If brought into intimate contact with mercury in presence of moisture, aluminium is readily converted into the hydroxide.

A mixture of aluminium powder and sodium peroxide will explode if moistened with a few drops of water.

A mixture of aluminium powder (paint flake) with finely ground potassium permanganate will burn with a bright flash if ignited.

Finely divided aluminium, when heated, will burn in halogens and in nitrogen.

Aluminium reacts very violently with a solution of bromine or iodine in dry ether, forming the bromide or iodide.

Sulphur, selenium and tellurium do not react with aluminium in the cold but combine with it on heating.

Red phosphorus combines directly with aluminium powder when the mixture is fired by means of magnesium ribbon. Arsenic and antimony also combine directly with aluminium on heating.

Hydrogen chloride attacks heated aluminium, forming the volatile chloride.

Chlorides of sulphur, selenium, phosphorus, arsenic, antimony or any chlorides which easily part with chlorine react readily with aluminium.

Carbon disulphide reacts with aluminium on heating, but hydrogen sulphide and ammonium sulphide have no action on the metal.

The action of a solution of hydrochloric acid depends on the purity of the metal and the strength of the acid. Aluminium of 99·99% purity will resist strong hydrochloric acid for many hours. Metal of normal commercial purity, say 99·5%, is rapidly dissolved.

Hydrobromic and hydriodic acids act similarly to hydrochloric acid.

Dilute hydrofluoric acid attacks aluminium with extreme rapidity, but very concentrated acid coats the aluminium with a layer of fluoride which checks further action.

Hypochlorous acid and hypochlorites attack aluminium slowly, producing pitting corrosion. Chloric acid also acts slowly on the metal and perchloric acid has no action.

Sulphuric acid only dissolves aluminium slowly when dilute; the attack increases as the acid strength increases and then diminishes again to a very small value for acid over 98% strength.

Sulphates of the alkalis have little action in water solution on aluminium, but the metal is precipitated by aluminium from aqueous solutions of the sulphates of such heavy metals as copper or silver.

When dry mixtures of the sulphates of the alkalis, alkaline earths etc., with aluminium powder are ignited, a vigorous or explosive reaction occurs.

Aluminium is attacked rapidly by aqueous solutions of potassium persulphate but more slowly by the ammonium salt.

Aluminium dissolves in an aqueous solution of phosphoric acid.

Nitric acid only attacks aluminium slightly and aluminium vessels can be used to transport concentrated nitric acid.

Ammonia solutions attack aluminium very slightly in the cold but much more vigorously when hot.

Caustic alkalis in solution, $NaOH$, KOH, or $Ba(OH)_2$, attack aluminium with great vigour; $Ca(OH)_2$ is not so vigorous in its action owing to its lower solubility.

Lead and zinc are precipitated from their solutions or fused salts by aluminium.

Silicates and borates are reduced on heating with aluminium.

Aluminium reduces selenious and tellurous acids in solution to selenium and tellurium.

Fused silver chloride is reduced to the metal by aluminium.

For the applications of aluminium to the chemical industry the main question is what substances can or cannot be used in contact with the metal. An extensive list of materials has been considered by H. Buschlinger in the Werkstoffbandbuch Nichteisenmetalle (published by the Deutschen Gesellschaft für Metallkunde im verein deutschen Ingenieure). This list, with some omissions, is given below.

The following signs are used :

Aluminium practically unattacked	+
Aluminium attacked slightly, or only in special circumstances	M
Aluminium attacked	—

Inorganic Substances.

Water. Distilled, hard, moor, and chalybeate	+
Sea-water, brine springs	—
Acids. Strong inorganic acids in solution, HCl, HF, H_2SO_4, H_2SO_3, HNO_3, H_3PO_4 over 1%, H_2SiF_6, titanic acid, and boric acid	—
Phosphoric acid under 1%	+
Nitric acid, concentrated	M
Halogen salts in solution. $NaCl$, $MgCl_2$, $ZnCl_2$, $BaCl_2$, KCl, $CaCl_2$, "chloride of lime"	—
Magnesium chloride dry	+
Aktivin (chloramine-T)	M
Sulphur compounds. Sulphur, SO_2, blast furnace gases containing sulphur compounds, ammonium sulphide	+
Sulphates in solution. Aluminium sulphate, alum, ferrous sulphate 1% and over, zinc sulphate, copper sulphate	—
Ferrous sulphate under 1%	+
Sodium sulphate dry	+
Aluminium sulphate dry	—
Nitrogen compounds. Ammoniacal solutions, ammonia-air mixtures, ammonium nitrate, nitrous gases, potassium nitrate and nitrite solutions, ammoniacal liquors of gas works after the washers	+
Ammoniacal gas works liquor before washing	—
Silicon chloride	—
Caustic alka'is, soda, caustic potash, and potassium silicate	—
Potassium chromate and bichromate solutions	+
Lime, milk of lime, concrete, mortar	—
Ferro- and *Ferricyanide* of potassium	—
Mercury and its salts	—

Organic Substances.

1. *Aliphatic compounds.* Hydrocarbons, methane, etc., petroleum, lubricating oil, asphalt, montan wax	+
Halogen derivatives. Ethylene trichloride, ethylene bromide, carbon tetrachloride dry	+
Carbon tetrachloride moist	—
Alcohols. Methyl alcohol, ethyl alcohol, propyl alcohol, amyl alcohol, etc., wort, distilled spirits, sour beer, brandy, liqueurs, etc.	+
Mashes	M
Wine making	—
Ethers, aldehydes, and ketones	+
Trichloracetaldehyde	—
Acids. Formic, acetic, butyric, valeric, oxalic, succinic, citric, lactic	—
Palmitic, stearic, tartaric, fruit juices, milk	+
Waxes. Beeswax	+
Oils and Fats. Neutral oils and fats	+
Nitrogen compounds. Trimethylamine, urea	—
Mustard, mustard oil, thiocyanates	+
Glycerin	+
Explosives industry. Nitroglycerin, lead azide	+
Fulminate of mercury	—
Carbohydrates. Sugar solutions, cellulose	+
2. *Carbon ring compounds.* Tar, heavy oil, toluol, naphthalene, anthracene benzol, illuminating gas, phenol carbolic acid, cresol, Lysol, Kreolin, Salveol, tricresol	+
Benzyl alcohol	+
Benzamide, anthranilic acid, salicylic acid, tannic acid	—
Terpentine, camphor, copal-gum, rubber	+
3. *Heterocyclic compounds.* Indole and pyrrole group	—
Natural alkaloids	+
Hard cheese	+
Soft cheese	—
Gelatine, glue	+

With further reference to the chemicals in contact with which aluminium or aluminium bronze is used the following information is taken from a paper by B. E. Roetheli and H. O. Forrest (Ind. Eng. Chem. 1932, **9**, 1018), summarising the replies from various firms concerning the materials used by them.

Chemical.	Plant.	
Nitric acid	Storage Reactors	Pure aluminium, acid below 20% or above 40%, no Cl, Br, or I ions or H_2SO_4 present.
Sulphuric acid	Pickling tubs Pumps	6% acid, aluminium bronze. Aluminium bronze.
Sulphurous acid	"	"

Chemical.	Plant.	
(Mono) Ammonium phosphate	Evaporators	Pure aluminium.
Ammonium sulphate	,,	,, ,,
Copper sulphate	Pumps	Aluminium bronze.
Potassium chloride	,,	,, ,,
Zinc nitrate	,,	,, ,,
Zinc sulphate	,,	,, ,,
Ammonia	Vapour lines	Pure aluminium, where no alkali salts present.
Potassium hydroxide	Storage	Aluminium bronze.
Sodium hydroxide	,,	,, ,,
Hydrogen sulphide	Gas piping (cold)	Pure aluminium.
Sulphur dioxide	Fans	Pure aluminium, aluminium bronze.
	Moist gas piping	Aluminium bronze.
Fruit juices	Evaporators Pipe Pumps	Pure aluminium.
Milk	—	Pure aluminium.
Acetic acid	Concentrators Condensers Piping	Pure aluminium, but there must be no halogen ions or formates present.
Acetic acid, glacial	Condensers	Pure aluminium.
	Pipes	,, ,, aluminium bronze.
	Pumps	,, ,, ,, ,,
	Reaction vessels	,, ,,
	Stills	,, ,,
	Storage	,, ,,
Benzoic acid	Piping	,, ,,
Citric acid	,,	,, ,, (for dilute acid).
Fatty acids (propionic, butyric, etc.)	Condensers	,, ,, aluminium bronze.
	Pumps	,, ,, ,, ,,
Phthalic acid (solution)	Evaporators	,, ,,
	Filters	,, ,,

Protection of Aluminium from Corrosion.—A highly tenacious film of oxide may be produced on aluminium by the process of Bengough and Sutton (Engineering, 1926, **122**, 274), in which the aluminium article is made anode in a bath containing 3% chromic acid as free as possible from sulphuric acid. The voltage is gradually raised to 40 volts in 15 minutes, kept constant for 35 minutes, raised to 50 volts during 5 minutes, and finally kept constant for 5 minutes. Protection may be improved by dipping in molten lanoline, or by coating with paint or varnish. The oxide coat may be dyed any colour. The process is also applicable to duralumin, zinc-aluminium alloys, silicon alloys up to 8·7% Si, and copper alloys containing less than 5% Cu. The oxide coating forms a good base for further protection by painting, as the paint adheres better to this oxide layer than it does to an ordinary metal surface. A simpler though not quite so effective process of coating is to boil the aluminium in a solution of 20 grms. sodium carbonate and 5 grms. potassium dichromate per litre of water, for 10 minutes. The paint finishes usually adopted for protecting sheet steel are satisfactory for aluminium. Aluminium paint made with varnish yielding a flexible paint film is also useful. In order to provide a material having great strength and the resistance of pure aluminium to corrosion, the Aluminium Co. of America have brought out a composite material named *Alclad*, consisting of a strong alloy sheet coated on each side with a layer of high purity aluminium. The alloy *K.S. Seewasser* is claimed by German authorities as being extremely resistant to the action of sea-water even when it is in contact with other metals, though Edwards, Frary, and Jeffries ("The Aluminium Industry") describe it as not necessarily better than certain older alloys such as the one containing 2% of manganese. In some cases sodium silicate is a valuable preventive of corrosion by alkaline materials where it may be added without detriment, as in the case of shaving creams, tooth-pastes, etc., where 0·1 0·3% of sodium silicate will stop the action on collapsible aluminium tubes, etc. Similarly sodium silicate with sodium carbonate or sodium phosphate may be used to clean aluminium, and sodium sulphide solutions can be prevented from action on aluminium by an addition of sodium silicate.

Aluminium Alloys (*see also* ALLOYS, LIGHT).—Attempts have been made to alloy aluminium with the following elements: antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, chromium, cobalt, copper, germanium, gold, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, niobium, phosphorus, platinum, potassium, selenium, silicon, silver, sodium, tellurium, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, zinc, zirconium.

Of these the following are almost completely insoluble in aluminium in the solid or liquid state and do not form compounds: bismuth, cadmium, lead, potassium, sodium, thallium.

Arsenic forms a compound insoluble in either molten aluminium or arsenic.

Beryllium, germanium, silicon, and tin form molten solutions with aluminium but do not form compounds. Zinc approaches these, as it forms a compound which is only stable over a restricted temperature range.

The remainder form one or more compounds and yield constitutional diagrams of notable complexity in some cases such as copper.

Of the binary alloys there are only two series of commercial importance, the copper-aluminium and the aluminium-silicon.

The rest of the commercial alloys are ternary, or more complicated, mixtures.

The table on p. 277 gives the more common alloys of which aluminium is the largest constituent and indicates clearly the seven elements which have been found to be effective in improving the mechanical properties of aluminium. It would be possible to extend the list to over 150 trade names for alloys which have been brought out at one time or another containing over 50% of aluminium, and it would be found that in general they contained one or more of the above seven elements in varying proportions, with small additions (less than 1%) of other elements. Some alloys have been claimed containing chromium up to 4%, others with tin up to 10%, and again 33% silver has been claimed in *Tiers Argent* and in smaller amounts in other alloys.

High silicon alloys are always used in the "modified" form in which the eutectic takes a very fine grained form. This is brought about by treating the molten alloy with about 0·05% of metallic sodium or potassium, or with sodium fluoride. Other agents which produce modification are potassium fluoride, lithium fluoride or double compounds containing fluorine and an alkali metal, caustic soda, alkaline earth metals and compounds, antimony compounds and boron compounds. The iron content should be low in these alloys, as it forms very large crystals of a brittle constituent $FeSi$ which weaken the alloy. These alloys give very good castings; the 5% Si alloy is said to be so free from porosity that castings may be used for high vacuum apparatus.

Many of the other aluminium alloys may be improved by heat treatment; these contain one or more compounds such as $CuAl_2$, silicides of Mg, Ca, Li and Zn, the solid solubility of which decreases as the temperature falls. The treatment consists of heating the alloy at a suitable temperature which may vary from 350° to 530° until the greatest possible amount of material has been taken into solid solution. The time of heating depends on the massiveness of the article and the method of heating, whether a sodium nitrate bath or an air bath is used. After heating, the article is quenched, giving an unstable solid solution from which the insoluble constituent separates in an extremely finely divided form, either spontaneously or on heating for some time to a temperature of 100°–200°. The practical result of this treatment is a great increase in strength and hardness. For example, the tensile strength of a duralumin may increase from 25,000 lb./in.^{2} in the annealed state to 50,000 lb./in.^{2} in the heat-treated form. Similarly an N.P.L. "Alloy E" (20% zinc, 2·5% copper, 0·5% magnesium, 0·5% manganese) may have a yield point of 32,500 lb./in.^{2} and tensile strength of 56,700 lb./in.^{2}, and after being quenched at 450° and aged they may become 65,000 lb./in.^{2} and 87,100 lb./in.^{2} respectively.

Other treatments to improve alloys are designed for the removal of dross and dissolved gases and the refinement of the grain size. Various fluxes have been patented for this purpose, usually mixtures of some of the following salts: $NaCl$, NH_4Cl, $ZnCl_2$, $6NaF \cdot Al_2F_6$, $LiCl$ and KCl. Nitrogen gas, or nitrogen and chlorine, or organic chlorine compounds, may be bubbled through the melt; this treatment removes gases and dross, but rather tends to increase grain size. Boron trichloride and titanium chloride remove gas and refine grain size. Another method of removing gas is to cool the molten alloy slowly through its freezing range till it is just solid, then remelt as rapidly as possible and cast immediately.

The table below indicates the strength-weight ratio for some materials (H. C. Knerr. Trans. Amer. Soc. Steel Treating, 1928, **13**, 723).

Metal.	Tensile strength, lbs./in.^{2}	Specific gravity.	Strength-weight factor.
Duralumin	55,000	2·80	19·3
25S. . .	55,000	2·80	19·3
Alloy steel	150,000	7·85	19·1
51S. . .	45,000	2·69	16·7
Steel . .	60,000	7·85	7·6
Brass, rolled	55,000	8·4	6·5
Aluminium (soft) .	12,000	2·7	4·4

An important part of the advantage of aluminium alloys as materials of construction is that they have a large section, relative to steel etc., for the same total tensile strength, and hence have greater stiffness.

In most of the alloys it is desired to obtain strength and lightness, but in some, such as aldrey or almalec and silmalec, a combination of good electrical conductivity (28–34 m./ohm/mm.^{2}) with considerable strength (25–40 kg./cm.^{2} tensile). These alloys are intended to provide an alternative to the usual steel-cored aluminium cable.

Aluminium Bronzes, Brasses, etc.—Aluminium bronzes are alloys of copper containing up to about 11% of aluminium. They have great strength and resistance to corrosion by acid media, except nitric acid. The following figures refer to specifications by the Society of Automotive Engineers, the American Society for Testing Materials, and the Air Ministry Specification DTD 197.

	Al.	Fe.	Ni.	Sn.
DTD197 .	8–12	4–6	4–6	
SAE . .	7–9	2·5–3·5		0–0·5
ASTM—A	7–9	2·5–4		0–0·5
ASTM—B	9·5–10·5	0–1·0		0–0·2

SOME ALUMINIUM ALLOYS.

(*a*) Alloys used principally in the wrought form.

Nominal Composition, Remainder Al.								Trade Names.
Si.	Cu.	Zn.	Mg.	Mn.	Fe.	Ni.		
2	4	—	—	—	—	—	—	Aeron, Lautal.
0·5–0·6	—	—	0·4–1·0	—	—	—	—	Aldrey, Almalec, Silmalec, 51ST.
0·8–2·0	—	—	0·8	—	—	—	—	Almasilium.
0·7–2·0	2·5–5·5	—	0·2–1·0	—	—	—	—	Aludur.
1·0	—	—	0·6	0·6	—	—	—	Anticorodal.
Up to 1·4	3·5–4·75	—	0·5–0·75	0·5–1·0	—	—	—	Avional.
Up to 0·55	1·0–2·0	5·0–9·0	Up to 4·0	Up to 1·0	—	—	Ti=0·5	Constructal.
—	4·0	—	0·5	0·5	—	—	—	Duralumin, 2L3, 17ST.
—	2·0–2·5	4·5–5·0	—	—	—	—	—	2L32.
—	3·5–4·5	—	1·2–1·7	—	—	1·8–2·3	—	L24, Y alloy, Birmidium.
1·2–2·8	1·0–3·0	—	0·1–1·8	—	1·1–1·4	2·0	Ti=0·08 to 0·20	Hiduminium, RR alloys.
0·8	5·0	—	—	0·8	—	—	—	25ST.
—	—	—	7	—	—	—	—	Hydronalium.
0·5–1·0	—	—	0·8–2·0	0·4–1·4	0·5–1·0	1·5	—	Pantal.
(*b*) Alloys used principally for casting.								
10–13	—	—	—	—	—	—	—	Alpax, M.V.C., Wilmil, Silumin, No. 47.
12	—	—	0·2–0·3	0·3–0·5	—	—	—	Silumin γ.
8–13	—	—	—	—	—	Up to 3·5	—	Birmasil.
14	0·9	—	1·0	—	1·0	2·5	—	Loex.
—	—	—	2·5	1·5–3·0	—	—	Sb=0·2 to 0·5	K.S.S.
—	6·0–8·0	—	—	—	—	—	—	3L11, American alloy, No. 12.
—	11–13	—	—	—	—	—	—	2L8.
—	2·5–3·0	12·5–14·5	—	—	—	—	—	2L5, Deutsche. Leg.
—	2·0–2·5	10	—	—	—	—	—	No. 145, Lynite.
—	9·5–10·5	—	0·45–0·55	—	0·4–1·0	—	—	Nelson Bohnalite, No. 122.
—	1·75	—	1·75	—	—	1·0	—	Magnalium No. 1.
—	—	—	3·5–5·0	0·5	—	—	—	Birmabright.
—	3·5–4·5	—	1·2–1·7	—	—	1·8–2·3	—	L24, Y alloy.

Iron, nickel and sometimes manganese are added to give increased strength. Lead or tin may be added to give ease of machining but they decrease the strength of the alloy. Silicon may also be added to reduce the hardness. The bronzes with about 9% and upwards of aluminium can be hardened by heating and quenching.

Special brass of high strength and elongation on fracture can have the composition 58·9% Cu, 38% Zn, 3·1% Al; manganese may also be present up to nearly 4% in alloys of this type.

Monel metal is strengthened when alloyed with a small amount of aluminium.

Some steels, to be hardened by nitriding, contain about 1–2% of aluminium as an alloying element.

Copper and nickel alloys used for electrical resistances may contain some 2% of aluminium; zinc base die-casting alloys may contain a small percentage of aluminium; while magnesium base light alloys may contain up to about 10% of aluminium.

Jointing of Aluminium.—Aluminium may be soldered with zinc, zinc-tin or zinc-cadmium alloy. These low melting solders must be used without a flux, by scraping, and the joint must be protected from moisture. Certain German hard solders are claimed to resist steam and water; these are mainly aluminium, containing small amounts of numerous other metals to lower the melting-point below that of aluminium. The best solders are the aluminium silicon alloys, which withstand steam or water.

The most satisfactory joint is obtained by welding, using an oxy-hydrogen or oxy-acetylene blowpipe, and there are satisfactory methods of welding bars or heavy wire by electrical resistance heating.

Heat-treated alloy sheets are joined by riveting.

Industrial Uses.—Aluminium and its alloys find application in the making of chemical apparatus for manufacturers, in brewing, in motor-car, aeroplane and airship construction, in cooking utensils, electrical machinery and power lines, in small parts for vacuum cleaners and the like, in cameras, in containers for food, in ornamental mouldings for architectural work and other purposes. Notable progress has been made in the use of aluminium alloys in motor bus and train work, as in these cases the reduction in weight due to replacing iron and steel by light alloys effects great saving in running costs and shows a profit after paying for the more expensive metal.

Other industrial products of aluminium are granules of various sizes for adding to molten steel, for Thermit reactions, and for explosives.

Aluminium foil, made by pack rolling thin sheet, is much used as a substitute for tin foil for wrapping foodstuffs and also for electrical condensers. Very thin foil is used for various decorative purposes such as book-binding, picture frames, etc. An interesting use for aluminium foil is the "Alfol" process of heat insulation, which employs layers of crinkled foil as thermal insulation (E. Schmidt, Z. Ver. deut. Ing. 1927, **71**, 1395), for which extreme efficiency is claimed and obviously the greatest economy in weight.

Aluminium Powder.—Aluminium powder for use in making paints or for decorative work in printing cannot be made by the usual processes of granulation by air or steam blasts or pouring into water. It is essential that the grains should be very fine and highly polished. Powder for paints is made by the following process: clippings of aluminium foil pounded in a stamp mill until they are reduced to a sufficiently fine powder are sieved, graded, and polished. The polishing machines take the form of drums lined with hard steel plates and having brushes fitted to an axle passing through the drum. The powder, mixed with about 2% of stearine or stearine and talc, is ground between the brushes and the drum and so acquires a very high polish. There is considerable risk of explosion and fire in this process, as the fine aluminium powder, like other inflammable dusts, *e.g.* coal dust, will form an explosive mixture with air.

Aluminium paint is made by mixing 2 lb. of the powder with a gallon of vehicle and thoroughly stirring; as it must be used as soon as possible, it is best to make it up fresh each day. The best vehicle is varnish of the long oil "spar varnish" type, which should have at least 50% by weight of non-volatile oils and gums, a viscosity between 0·5 and 1·00 poise, and should pass a 30% Kauri reduction test. With such a vehicle a proportion of the powder floats to the surface layer of the paint after it is applied, owing to some surface tension effect; this effect is called "leafing"—the grains are flat flakes and collect more or less parallel to the surface. This result gives the brightest appearance and is best obtained when the paint is freshly made with the correct vehicle.

For work where the greatest resistance to exposure to weather is not required various vehicles may be used. Pyroxylin lacquers give a different appearance, as the flakes in these do not give the "leafing" effect, but remain indiscriminately oriented.

Other aluminium products are *Alclad*, already mentioned under the protection of aluminium from corrosion (p. 275), and *Feran*, which consists of iron sheet coated on each side with aluminium sheet by a special rolling process, the object being to combine the strength of iron with the corrosion resistance of aluminium.

Plating on aluminium.—Owing to the oxide skin on aluminium difficulties arise in securing adhesion for the deposit. To overcome this trouble the surface of the aluminium is etched with a solution containing hydrochloric acid and nickel chloride, iron chloride or manganous sulphate or, in the case of some alloys, a mixture of strong nitric acid and strong hydrofluoric acid. The correct strength of etching solution depends on the purity of the aluminium and must be gauged by experience. After the etching bath the aluminium is plated with nickel, which forms the basis for plating any other metal if required.

Polishing aluminium.—For a good finish on commercial articles the grain size of the final polishing material should be very small; anything more than a trace of material, say 0·2%, over 90 mesh will cause scratches ; the bulk should pass 200 mesh. No rouge or dark material should be used.

BOOKS AND PAMPHLETS RELATING TO ALUMINIUM.

J. Billiter, "Technische Elektrochemie," Halle-Saale, 1923–1932.

"Light Metals and Alloys," Circular of Bur. Stand., No. 346 (U.S. Government Printing Office).

P. Melchior, "Aluminium die Lichtmetalle und ihre Legierungen," V.D.I.-Verlag.

Allmand, "The Principles of Applied Electrochemistry," Edward Arnold & Co., London.

"Traité de Chimie Minérale," publié sous la direction de Paul Pascal, Tome VII, Masson et Cie.

W. H. J. Vernon, "A Bibliography of Metallic Corrosion," Edward Arnold & Co., London, 1930.

M. G. Corson, "Aluminium and its Alloys," Chapman & Hall, London, 1926.

Edgar T. Painton, "The Working of Aluminium," Chapman & Hall, London, 1927.

G. L. Mantell, "Industrial Carbon," Chapman & Hall, London, 1928.

J. D. Edwards, "Aluminium Bronze Powder and Aluminium Paint," Chem. Catalog Co., New York, 1927.

Cyril S. Fox, "Bauxite," Crosby Lockwood, 1927.

R. J. Anderson, "Secondary Aluminium," London, 1933.

H. F. Budgen, "Heat Treatment and Annealing of Aluminium and its Alloys," Chapman and Hall, Ltd.

A. von Zeerleder, "Technologie des Aluminiums und seiner Leichtlegierungen," Akademische Verlagsgesellschaft, Leipzig.

Victor Engelhardt, "Handbuch der technischen Elektrochemie," Vol. III, Akademische Verlagsgesellschaft, Leipzig, 1934.

V. Fuss, "Metallographie des Aluminiums und seiner Legierungen," Julius Springer, Berlin, 1934.

J. H. Burn, "Aluminium and Food," British Non-ferrous Metals Research Association.

"A Select Annotated Bibliography on the Hygienic Aspects of Aluminium and Aluminium Utensils," Mellon Institute of Industrial Research.

Georg Günther, "Die Deutsche Rohaluminium Industrie," Curt Bottger.

"L'Aluminium dans les Industries Chimiques et Alimentaires et Industries connexes," Bureau International de l'Aluminium, Paris.

D. M. F.

ALUMINIUM, DETECTION AND DETERMINATION OF.

The processes employed and the errors involved in the quantitative determination of aluminium in its compounds, in rocks, bauxite, glass, and refractories are admirably described by W. F. Hillebrand and G. E. F. Lundell ("Applied Inorganic Analysis," New York, 1929) and by F. P. Treadwell and W. T. Hall ("Analytical Chemistry," 8th ed., Vol. II, New York, 1935); metallurgical practice by W. A. Naish and J. E. Clenell ("Select Methods of Metallurgical Analysis," London, 1929) and by G. Lunge and C. A. Keane ("Technical Methods of Chemical Analysis," Vol. II, 2nd ed., London, 1928) ; and the determination in flour, foods, and other natural products in A. H. Allen's "Commercial Organic Analysis" (5th ed., Index Vol. X, London, 1933 ; *see also* G. W. Monier-Williams, Reports on Public Health, No. 78, H.M. Stationery Office, London, 1935). Colorimetric methods using aluminon, alizarin S, and hæmatoxylin are adequately treated in J. H. Yoe's "Photometric Chemical Analysis" (Vol. I, New York, 1928, 109–122; *see also* Snell, "Colorimetric Methods of Analysis," vol. I, London, 1936 ; *cf.* P. S. Roller, J. Amer. Chem. Soc. 1933, **55**, 2437). The gravimetric and volumetric determination with 8-hydroxyquinoline (oxine) is given by A. D. Mitchell and A. M. Ward ("Modern Methods in Quantitative Chemical Analysis," London, 1932 ; *see also* H. B. Knowles, Bur. Stand. J. Res. 1935, **15**, 87). More recent volumetric and gravimetric processes are referred to by C. A. Mitchell (Recent Advances in Analytical Chemistry, Vol. II, London, 1931), and full references are given, to July 1934 in Gmelin's Handbuch (System Nr 35, *A*, 431–447) and to the end of 1935 in the Chemical Society Annual Report (L. S. Theobald, "Inorganic Analysis," 451–475).

A spectrophotometric method is described by F. Alton, H. Wieland, and E. Knippenberg (Z. anal. Chem. 1934, **96**, 91), and spectrographic analysis is discussed by Gerlach (Angew. Chem. 1933, **46**, 557), H. E. S. van Somern (J. Inst. Metals, 1934, **55**, 265) and D. M. Smith (*ibid.* 1935, **56**, 119).

In the ordinary course of qualitative analysis aluminium is obtained as the hydroxide by precipitation with aq. ammonia in presence of ammonium chloride (F. T. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. I, 1935). Formerly its presence was confirmed by moistening a little of the hydroxide with very dilute cobalt nitrate, and heating it before the blowpipe, when a blue coloration (Thénard's Blue) was produced. In spite of the improved technique devised to enhance the sensitivity of this test (Gemmill, Brackett and McCosky, J. Amer. Chem. Soc. 1929, **51**, 1165 ; Otto, *ibid.* 1926, **48**, 1604), it has generally given place to the more specific and delicate precipitation or colour reactions (*e.g.* with morin or aluminon) described below amongst the *micro-chemical methods*. Other reactions are given by Treadwell and Hall (*l.c.*) and by R. R. McAlpine and B. A. Soule ("Qualitative Chemical Analysis," London, 1933).

Micro-methods employed in detecting aluminium are dealt with by F. Feigl ("Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 2nd ed., Leipzig, 1935, 236–242; *see also* Chem. Soc. Annual Reports). To detect **Al** with morin ($C_{15}H_{10}O_7,2H_2O$) in the presence of metals which also give colours or precipitates with the reagent, these metals are removed by precipitation with a slight excess of 2*N*- **KOH** ;

the centrifuged, clear solution is transferred to a small test-tube or to a black tile, acidified with 2*N*– acetic acid, and treated with a drop of morin solution (satd. soln. in $CH_3{\cdot}OH$). A green fluorescence indicates Al. The sensitivity of the test is 0·2γ (0·2×10^{-6} g.) of Al, and the limiting dilution 1 : 250,000. The sensitivity of the test is said to be increased to 0·005γ of Al and the limiting dilution to 1 : 10,000,000 by impregnating a filter paper with morin solution, drying it, adding the drop of test solution, re-drying, and treating with several drops of 2*N*– HCl. In the presence of Al, a brilliant light green fluorescence appears in ultra-violet light.

Alizarin S yields a red lake with Al compounds in alkaline solution. A drop of the alkaline Al solution (not more than *N*– with respect to alkali) is treated with a drop of alizarin S solution (0·1% aq. Na alizarin sulphonate), and *N*– acetic acid is added until the violet colour disappears, then one drop is added in excess. According to the quantity of Al present, a red precipitate or coloration is produced. The sensitivity is 0·65γ of Al, and the limiting dilution 1 : 77,000 (*cf.* S. N. Polschinok, J. App. Chem. Russia, 1933, **6**, 948).

The lakes obtained with alizarin, quinalizarin (Feigl, *l.c.*), and alkanet (H. W. Estell and R. L. Nugin, J. Amer. Chem. Soc. 1927, **49**, 1991 ; F. Alton, H. Wieland, and H. Loofman, Angew. Chem. 1933, **46**, 668) also lend themselves to extremely sensitive qualitative tests. The red lake with ammonium aurinetricarboxylate (*aluminon*) is sensitive to 1γ (*see* B.D.H. Reagents for Spot Tests, London, 1934). Unfortunately Be, rare earths, Zr, and Th (A. R. Middleton, J. Amer. Chem. Soc. 1926, **48**, 2125) also yield red flocculent precipitates which are only decolorised by aq. ammonia–ammonium carbonate with difficulty.

Other tests depend on the formation of the slightly soluble cæsium alum (H. Yagoda and H. M. Partridge, *ibid.* 1930, **52**, 3579), or of the rose-pink coloration with eriochromcyanin R (E. Eegriwe, Z. anal. Chem. 1929, **76**, 438).

The determination of Al on the micro-scale may be successfully carried out with 8-hydroxyquinoline after the removal of metals which interfere (A. Benedetti-Pichler, Mikrochem. 1929, Pregl Festband, 6).

ALUMINIUM, COMPOUNDS OF.

The pure chemistry of aluminium compounds is treated in the following major works: J. W. Mellor, "A Comprehensive Treatise on Inorganic and General Chemistry," Vol. V, London, 1923, *cited* as Mellor, Vol. V ; J. N. Friend, "A Textbook of Inorganic Chemistry," Vol. IV, London, 1921, *cited* as Friend, Vol. IV ; and Gmelin's "Handbuch der anorganischen Chemie," 8th ed., System Nr. 35, Aluminium, Teil *A*, Berlin, 1934 ; the Appendix to Teil *A*, Aluminium Legierungen, Patentsammlung, Berlin, 1936 ; and Teil *B*, Berlin, 1933–1934, *cited* as Gmelin, System Nr. 35, *A* ; *A* Pat. ; and *B* respectively. The handbook contains in addition to the pure chemical aspects an outline of the more important industrial processes involved in the preparation and application of aluminium and its compounds, and give in an easily accessible form a complete set of references to the ordinary scientific and to the patent literature. A general outline of industrial practice, especially in Germany, may be found in Ullmann's Enzyklopädie der technischen Chemie, 2nd ed., Vol. I, Berlin, 1928, *cited* as Ullmann, **1**. Specific references are given in the appropriate places in the text.

Aluminium and hydrogen.—A stable compound of aluminium and hydrogen has not been prepared, but in suitable circumstances the metal takes up various proportions of hydrogen, and is therefore grouped by G. F. Hüttig with the elements forming metal-like hydrides. In the course of its production and treatment aluminium takes up gases (chiefly hydrogen and nitrogen) usually in such quantity that their total volume is from 7 to 20% of that of the metal. Good metal tapped from the reduction furnaces yields 5 to 10% of its volume of hydrogen and about 3 to 4% of nitrogen. After re-melting, especially under unsuitable conditions, it is found to contain more hydrogen and also carbonic oxide and hydrocarbons. An ingot of metal which had been melted and allowed to cool in the furnace very slowly was highly crystalline and found to contain no less than 85% hydrogen, 7·5% nitrogen, and 4% carbonic oxide and hydrocarbons. Between 900° and 1,500° molten aluminium absorbs hydrogen in quantities increasing linearly to 35 vol.-%, with changes in certain of its mechanical properties (J. Czochralski, Z. Metallk. 1922, **14**, 277 ; L. L. Bircumshaw, Phil. Mag. 1926 [vii], **1**, 510), and considerable absorption may occur in the Al electrodes of discharge tubes, but the occurrence of a stable compound is as unlikely here (K. Rottgardt, Ann. Phys. 1910 (4), **33**, 1193) as it is on an Al cathode during the electrolysis of distilled water (E. Duter, Compt. rend. 1889, **109**, 109). A *molecule*, AlH, has, however, been identified by its emission and absorption spectra. It occurs in an arc between Al electrodes in an atmosphere of hydrogen at low pressures (G. Eriksson and F. Hulthén, Z. Physik, 1925, **34**, 780), and when an Al wire is exploded in hydrogen (H. Nagashima, Sci. Rep. Tokyo Bunrika Daigaku, 1932, **1**, 219) ; and it has been detected in the sun (R. S. Richardson, Astrophys. J. 1931, **73**, 231), and in the stellar spectrum of o-Ceti (R. Wildt, Z. Physik, 1929, **54**, 867 ; A. H. Joy, Astrophys. J. 1926, **63**, 281). L. Farkas (Z. Physik, 1931, **70**, 733) investigated the thermal equilibrium between Al vapour, hydrogen, and AlH in a porcelain tube between 1,500° and 1,700°. The application of Nernst's formula to the data gave the following values for the partial pressures of AlH at different hydrogen pressures and at 1,500° :

mm. H_2	15	100	760
mm. AlH	0·05	0·13	0·35

The band spectrum of AlH has been widely investigated (Gmelin, System Nr. 35, *B*, 1–4).

The moment of inertia I and the nuclear

distances r for the ground state $^1\Sigma$, and for the states $^1\Pi$, $^1\Sigma'$, and $^1\Sigma''$ are :

State	$^1\Sigma$	$^1\Pi$	$^1\Sigma'$	$^1\Sigma''$
I (10^{-40} g.cm.^{2})	4·338	4·331	4·17	4·23
r (Å)	1·651	1·650	1·62	1·63

The energy of dissociation of the molecule in the normal state is 3·07 volts (D. S. Villars and E. V. Condon, Physical Rev. 1930 [ii], **35**, 1031) or 70 kg.-cal. (L. Farkas, *l.c.*).

Aluminium suboxides.—A number of ill-defined suboxides, which were given the formulæ Al_2O, Al_4O_3, and Al_6O_7, are described in the earlier literature, but their existence has not been authenticated. The band spectrum of the *molecule* AlO is, however, easily observed and has been extensively investigated (R. S. Mulliken, Physical Rev. 1925 [ii], **26**, 570). It is excited in flames to which Al compounds have been added, in arc or spark discharges operating in the ordinary way, in discharge tubes, or under liquids, and its presence in the sun-spot spectrum is highly probable (R. S. Richardson, Astrophys. J. 1931, **73**, 229). The moment of inertia I and nuclear distance r (infinitely small vibrations) for the beginning and end states of the molecule are respectively I $46{\cdot}02\times10^{-40}$ g.cm.^{2}, r 1·665Å, and I $43{\cdot}38\times10^{-40}$ g.cm.^{2}, r 1·617Å, and the energy of dissociation of the molecule 95 kg.-cal. per mol. (R. Wildt, Z. Physik, 1929, **54**, 858).

Aluminium oxide, alumina, Al_2O_3.—The technical preparation of alumina from bauxite and other materials, and its natural occurrence have already been described (page 265). In the laboratory it is usually prepared by strongly heating the washed, precipitated hydroxide. An exceptionally pure, finely-divided oxide, which is now exclusively used in the preparation of artificial gems, results from the ignition of ammonium alum. Other alums and most Al compounds yield the oxide on ignition in the air, in the presence or absence of other substances, but they do not lend themselves to the preparation of the pure oxide. Aluminium vaporised in an electric arc and oxidised in an air blast yields a highly dispersed alumina which may be precipitated electrostatically (V. Kohlschütter and J. L. Tüscher, Z. Elektrochem. 1921, **27**, 250). Crystalline alumina (corundum) occurs native : colourless as hyaline, corundum, and leuco-sapphire, or coloured by metallic oxides as ruby (red), sapphire (blue), topaz (yellow), oriental amethyst (violet), oriental hyacinth (red-brown), oriental smaragd (green), oriental chrysolith (yellow-green), or oriental aquamarin (blue-green). Crude alumina, dark, and usually associated with magnetite and hæmatite, occurs in large boulders in many districts, and is used as a polishing and grinding medium in the form of *emery* (*q.v.*). Corundum may be prepared by allowing alumina which has been melted in the electric furnace or oxy-hydrogen blowpipe to crystallise. Fusion may be assisted by the addition of other substances, *e.g.* K_2S, Pb_3O_4, Al_2S_3, K_2MoO_4, $MgCO_3$, cryolite and $MgCO_3$, nepheline, SiO_2, $BaCO_3$, CaO and SiO_2, glass, or borax. Borax seems particularly suitable, since it partly volatilises after complete fusion, leaving behind the crystalline alumina in a water-soluble matrix. The occurrence of small corundum crystals in the slag from thermite reactions is well known, and O. Hönigschmidt (Monatsh. 1907, **28**, 1108) prepared them by igniting a mixture of 100 grms. of melted and powdered borax, 100 grms. of aluminium filings, and 125 grms. of sulphur flowers. Large, well-formed crystals have been obtained by heating Al fluoride to whiteness in a covered carbon crucible which contains a small platinum crucible filled with boric acid. The boric acid and Al fluoride react in the vapour phase forming alumina which deposits in pure crystals having the properties of natural corundum. Preparations based on similar principles consist in decomposing the vapour of Al chloride or fluoride at high temperatures with water vapour or lime, or in heating a mixture of equal parts of alumina and Ba or Ca fluoride or of cryolite and various silicates, in a closed crucible for a long period, when the corundum crystallised out on the walls. Small crystals have also been obtained by heating in sealed tubes aqueous solutions of Al chloride; Al chloride and an alkali carbonate; Al sulphate and urea; or an aqueous suspension of $Al(OH)_3$.

The preparation of large, single crystals for cutting as gems and instrument bearings has received considerable attention : (C. Doelter, Edelsteinkunde, 2nd Ed., Veit, Leipzig, 1909 ; M. Bauer, Edelsteinkunde, 2nd Ed., C. H. Tauchnitz, Leipzig, 1909 ; H. Michel, Die künstliche Edelsteine, 2nd Ed., W. Diebener, Leipzig, 1926 ; F. Krauss, Synthetische Edelsteine, G. Stilke, Berlin, 1929 ; I. H. Levin, Ind. Eng. Chem. 1913, **5**, 495 ; Gmelin's Handbuch, System Nr. 35, *B*, 10–12, 87–90.) The method consists in principle of strewing (*Streu-Verfahren, semage*) fine alumina powder at regular intervals on a very small surface, where, after melting in a particular zone of the oxy-hydrogen flame, it solidifies in layers to form a large, uniformly oriented crystal (A. Verneuil, Compt. rend. 1902, **135**, 791 ; Ann. Chim. Phys. 1904 [viii], **3**, 20). The operation is conducted in a furnace which consists of an oxyhydrogen blowpipe directed downwards surrounded by a refractory mantle provided with observation windows. Alumina is fed to the flame from a sieve, shaken at regular intervals, situated in the oxygen lead, and deposits on the upper end of a thin vertical rod of refractory material arranged in the axis of the flame. The alumina sinters to a conical pile from which a fine pencil grows upwards until its tip reaches a hotter zone of the flame where it fuses to a globule and, at the expense of the alumina in the flame, grows steadily to a large single crystal ultimately weighing from 10 to 50 g.

Numerous modifications have been employed to ensure a favourable orientation of the optical axes, the absence of inner strain, inclusions, and non-homogeneity, and to economise in alumina. The carrying rod may be rotated centrally (Elektrochemische Werke G.m.b.H., O. Dreibrodt, G.P. 284258, 1914 ; H. Michel, Chem. Zentr. 1927, **1**, 2590), or eccentrically

(O. Ruff, G.P. 395419, 1922) with reference to the blowpipe axis ; the mantle may be rotated (E. Schlumberberger, G.P. 390796, 1923) ; several centrally directed blowpipes may be used (*idem*. G.P. 390795, 1923) ; or the blowpipe may be supercharged with oxygen (Swiss Jewel Co. Soc. An., Swiss P. 135175, 1927 ; G.P. 524985, 1927). Strains have been released by annealing the finished crystals (I.G. Farbenind. A.-G., F.P. 666940, 1929), and a smooth surface has been induced by a short treatment with molten borax (I.G. Farbenind. A.-G., H. Espig, and W. Teubner, F.P. 689679, 1930). Loss of alumina may be mitigated by electrically charging the blowpipe head and carrying rod (M. Lange, G.P. 332390, 1919), whilst special arrangements have been described for admitting Al compounds to the flame (Siemens-Schuckertwerke A.-G., F.P. 644592, 1927 ; R. Nacken, G. Jaeger, and W. Grahmann, E.P. 245132, 1926).

The colours of the naturally occurring corundum gems are certainly due to the presence of small amounts of metallic oxides (C. W. Stillwell, J. Physical Chem. 1926, **30**, 1458 ; J. Papish and W. J. O'Leary, Ind. Eng. Chem. Anal. Ed., 1931, **3**, 13) and may be emulated in the artificial varieties by mixing the appropriate powdered metallic oxides with the alumina before admitting it to the flame: the red colour of rubies requires 2½% of Cr_2O_3 (A. Verneuil, Ann. Chim. Phys. 1904 [viii], **3**, 36) ; sapphire blue, 1·5% Fe_3O_4 and 0·5% TiO_2 (L. Heller and Son, U.S.P. 988230, 1910 ; 1004505, 1911) ; the lemon to brown-yellow tints, Ni oxide (L. Paris, Compt. rend. 1908, **147**, 933 ; A. Verneuil, *ibid.* 1908, **147**, 1059) ; the gold to brown of topaz, Ni and Mn oxides ; the orange to reddish-yellow, strongly dichroic padparadschah, Ni and Cr oxides ; green varieties, similar to epidote or smaragd, by adding Ni, Fe, and Ti oxides (Elektrochemische Werke, G.m.b.H., O. Dreibrodt, H. Espig, and D. Strausz, G.P. 385374, 1922), or Ni, Co, and V oxides (Swiss Jewel Co. A.-G., F.P. 666157, 1928).

The colour of natural or artificial rubies is little affected by radioactive or by ultra-violet radiation, but permanent changes have been observed in a number of colourless, yellow, and blue sapphires.

When heated, rubies and sapphires become green, and finally pale yellow or colourless, but by heating the artificial reddish-yellow gems immersed in sand to bright redness for 8 to 12 hours their colour may be permanently deepened (I.G. Farbenind. A.-G., Swiss P. 140037, 1928).

Considerable quantities of corundum are also made for use as abrasives and refractories. Bauxite is calcined, milled, mixed with the proper amount of carbon, and fused in an electric furnace. Iron oxides, silica, and a part of the titania are thereby reduced and melted, forming a heavier layer beneath the fused alumina. In the intermittent process (for furnace construction, *see*, *e.g.* R. Schneidler, Chem.-Ztg. 1930, **54**, 625 ; Tonind.-Ztg. 1932, **56**, 105 ; Feuerfest, 1932, **8**, 129), which appears to be favoured, after the charge has been adequately heated, the electrodes are withdrawn, and the furnace allowed to cool until the alumina solidifies as a block, which is lifted from the still liquid lower layer. The corundum is finally ground and graded according to size. It may be used directly as an abrasive, or mixed with a bonding material such as sodium silicate, rubber composition, or plastic clay, and fashioned into cutting wheels, whetstones, refractory bricks, or shapes (*e.g.* Siemens-Schuckertwerke A.-G., E.P. 382071, 1931 ; H. Kohl, Tonind.-Ztg. 1932, **56**, 1266 ; H. Gerdien, Z. Elektrochem. 1933, **39**, 13). Alundum laboratory ware is bonded with ball-clay and felspar and fired in a porcelain kiln.

The colour of these corundum varieties varies from white to dark brown or almost black according to purity. The density is 3·9. The hardness, about 9, varies with the method of manufacture, and alone is an insufficient criterion of the abrasive qualities of the specimen (H. Danneel, Chem. Fabr. 1928, **1**, 164 ; Werkzeug, 1928, **4**, 435).

Physical properties.—The heat of formation of alumina is 380·8±0·4 kg.-cal. at constant pressure. It is polymorphous, and five different forms have been identified. The *rhombohedral α-form* is the naturally occurring and the most commonly met modification. Its properties are discussed in detail below.

The *hexagonal* β-Al_2O_3 (G. A. Rankin and H. E. Merwin, J. Amer. Chem. Soc. 1916, **38**, 568 ; S. B. Hendricks and L. Pauling, Z. Kryst. 1926, **64**, 303) is stable at higher temperatures, the transformation $\alpha\text{-}Al_2O_3 \rightarrow \beta\text{-}Al_2O_5$ being complete at 1,500°-1,800° (V. M. Goldschmidt, T. Barth, and G. Lunde, Skr. Akad. Oslo, 1925, No. 7, 24). The density is 3·30, and the refractive indices n_ω 1·665-1·680, and n_ϵ 1·629-1·650 (Rankin and Merwin, *l.c.*).

A *cubic* γ-Al_2O_3 (W. Biltz and A. Lemke, Z. anorg. Chem. 1930, **186**, 373 ; W. C. Hansen and L. T. Brownmiller, Amer. J. Sci. 1928 [v] **15**, 229) results when natural or precipitated Al hydroxide is dehydrated below 950°. At higher temperatures it passes monotropically into α-Al_2O_3. γ-Al_2O_3 is distinguished by being highly dispersed, very hygroscopic, and easily soluble in acids (C. D. Bejankin and N. Delaktorsky, C. Min. 1932, A, 229). Its density is 3·42-3·647, and its refractive index 1·696±0·003.

Cubic δ-Al_2O_3 is formed by heating crystalline $AlCl_3,6H_2O$ to 180°. At 580° this passes into a well-crystallised form showing hexagonal or rhombohedral symmetry, and above 950° is transformed into the α-form (Biltz and Lemke, *l.c.* ; N. Parravano and V. Montoro, Atti R. Accad. Lincei, 1928 [vi], **7**, 885 ; 1929 [vi], **10**, 475). δ-Al_2O_3 is characterised by a low density, 2·38-2·40, and high powers of adsorption.

Cubic ζ-Al_2O_3 crystallises in regular octahedra from molten alumina or Al silicate containing lithia (H. B. Barlett, J. Amer. Ceram. Soc. 1932, **15**, 362). It has *d* 3·6, and n_D 1·736.

X-rays reveal that α-Al_2O_3 has a rhombohedral crystal lattice (D51-type, similar to Fe_2O_3 and Cr_2O_3), in which the aluminium atoms are equidistant from the centre on the vertical axis, and the oxygen atoms set in an equilateral triangle on the hexagonal axis (L. Pauling and S. B. Hendricks, J. Amer. Chem. Soc. 1925, **47**, 787 ; E. A. Harrington, Amer. J. Sci. 1927 [v], **13**, 470 ; W. H. Zachariasen, Skr. Akad. Oslo, 1928, Nr. 4, 15). The majority of density determinations lie between 3·95 and 4·00. The hardness is 9, being next to that of diamond. The compressibility is $0{\cdot}38$–$0{\cdot}43\times10^{-12}$ rec. dyne/cm.^{2} (E. Madelung and R. Fuchs, Ann. Phys. 1921 [iv], **65**, 307). Various values have been obtained for the linear coefficient of thermal expansion, of which the following are representative : parallel to the principal axis, at 20°–100° $6{\cdot}87\times10^{-6}$, at 20°–500° $8{\cdot}33\times10^{-6}$, at 20°–1,000° $9{\cdot}03\times10^{-6}$; perpendicular to the axis, at 20°–100° $5{\cdot}5\times10^{-6}$, at 20°–500° $7{\cdot}70\times10^{-6}$, and at 20°–1,000° $8{\cdot}31\times10^{-6}$ (J. B. Austin, J. Amer. Ceram. Soc. 1931, **14**, 799). The melting-point has been accurately determined to be 2,050° (*see* K. J. A. Bonthron and R. Durrer, Z. anorg. Chem. 1931, **198**, 142). The vapour pressure was determined by O. Ruff and M. Konschak (Z. Elektrochem. 1926, **32**, 518 ; cf. F. Born, *ibid.* 1925, **31**, 311) :

Temp. °C.	2,360	2,410	2,490	2,547	2,580
Press. mm. Hg	6	18	22	50	53

The results give on extrapolation a boiling-point 2,980° ± 60, and substituted in the Clausius-Clapeyron equation give a latent heat of vaporisation of 115·7 cal. The true specific heat varies with absolute temperature as follows :

T° (Abs.)	91·1	200·1	275·1	291·1
Sp. Heat	0·0249	0·1218	0·1726	0·1813

T° (Abs.)	373·1	573·1	773·1	973·1
Sp. Heat	0·2150	0·2538	0·2769	0·2832

(G. S. Parks and K. K. Kelley, J. Physical Chem. 1926, **30**, 51 ; W. A. Roth and W. Bertram, Z. Elektrochem. 1929, **35**, 304 ; *see also* A. B. Newman and G. G. Brown, Ind. Eng. Chem. 1930, **22**, 998). The thermal conductivity in cal. cm. sec. degree is at 16·7° 0·0466, at 200° 0·0255, at 500° 0·0169, and at 900° 0·0127 (H. Gerdien, Z. Elektrochem. 1933, **39**, 16), while values of the order 0·001 have been obtained for impure commercial specimens. Alumina is feebly double refracting, and the indices (Na light) are respectively n_ω 1·7689 and n_ϵ 1·7609.

Chemical properties.—Alumina is unaffected by hydrogen, but reacts with N at high temperatures in presence of C to form AlN. F, Cl, and Br react with Al_2O_3 in presence of C at high temperatures to form the respective Al halides. At very high temperatures it is reduced by C to yield Al carbide and the metal, while Na, K, Ca, Be, and Mg also reduce it to the metal under appropriate conditions. W reacts at 2,000° to give WO_2. HF and HCl, especially in presence of C, give the respective Al halides. H_2S and CS_2 yield Al_2S_3 at bright red heat ; S_2Cl_2, $SiCl_5$, PCl_5, BCl_3, CCl_4, and $COCl_2$ yield $AlCl_3$; Ni, Co, and Fe^{II} oxides, and alkali and alkaline earth oxides or salts with volatile anions, give aluminates ; other salts such as Na_2S, $KHSO_4$, $CaSO_4$, CaC_2, react in a similar fashion.

The solubility of Al_2O_3 in acids and alkalis varies considerably with its thermal history. Strongly calcined, it is scarcely attacked, and is only dissolved by sulphuric acid (8 : 3) on heating in a sealed tube. Finely dispersed, gently calcined γ-Al_2O_3 is, however, easily soluble (W. Biltz and A. Lemke, Z. anorg. Chem. 1930, **186**, 377, 381 ; G. F. Hüttig and A. Schaufel, Kolloid-Z. 1931, **55**, 201, 203).

Al_2O_3 dissolves in water to the extent of about 1×10^{-5} mol. litre at 20°, and $0{\cdot}96\times10^{-5}$ mol. litre at 29° (W. Bush, Z. anorg. Chem. 1927, **161**, 169).

Higher oxides.—A precipitate is obtained by adding 30% hydrogen peroxide solution to concentrated K aluminate solution. After washing and drying it is a light, amorphous powder with the composition $Al_2O_3,Al_2O_4,10H_2O$, soluble in acids and alkalis, and possessing oxidising properties (A. Terni, Atti R. Accad. Lincei, 1912 [v], **21**, ii, 104). Similar substances have been prepared technically by the electrolytic precipitation of Al salts in presence of oxygen (Henkel et Cie, G.P. 302735, 1914).

Aluminium hydroxide (F. Adickes, Z. angew. Chem. 1928, **41**, 1333 ; A. Simon, Kolloid-Z. 1928, **46**, 161 ; W. Biltz and G. A. Lehrer, Z. anorg. Chem. 1928, **172**, 305 ; R. Willstätter, H. Kraut, and K. Lobinger, Ber. 1928, **61** [B], 2283 ; V. Kohlschütter, Helv. Chim. Acta, 1931, **14**, 345).—Aluminium hydroxide exists in gelatinous and crystalline forms, and as a sol The rapid precipitation of $Al_2(SO_4)_3$ solutions with a slight excess of ammonia, and at low OH' concentration, yields the *a-orthohydroxide*, $Al(OH)_3$, a white, flocculent, amorphous gel, which transforms in a few hours to the *β-orthohydroxide*, ($[4Al(OH)_3-3H_2O]+2H_2O$), a faintly yellow, compact, plastic gel, which in its turn, after a few months, becomes the stable *γ-orthohydroxide*, a white, flocculent, glutinous gel of composition $Al(OH)_3$. The reactivity towards acids and bases diminishes from the α to the γ forms ; the adsorptive powers of α- and γ- are greater but less selective than those of the β-form.

By precipitating in the presence of an excess of ammonia, the pale yellow, plastic *dihydroxide*, $2Al(OH)_3,H_2O$, is obtained, which on heating above 60° passes into the stable, reddish-yellow *A-polyhydroxide*, $4Al(OH)_3,3(3{\cdot}5)H_2O$.

The ortho- or poly-hydroxides heated in sealed tubes with NH_3 solution yield the plastic, stable *metahydroxide*, AlO,OH.

All Al hydroxide gels appear to belong to one or other of these varieties, *e.g.* those prepared by allowing amalgamated Al to react with moist air, with concentrated $Ba(NO_3)_2$, or ammoniacal NH_4NO_3 solutions, or the gels of reproducible properties formed by the electrolysis of alkali salt solutions using an Al anode (V. Kohlschütter and M. Berlin, Helv. Chim. Acta, 1931, **14**, 3 ; Kohlschütter and W. Beutler, *ibid.* 1931, **14**, 305, 330).

Aluminium hydroxide gels, particularly when partly dehydrated at temperatures between 200° and 500°, are excellent drying agents, adsorbents, and catalysts, and their preparation and application are the subjects of numerous publications and patents (Gmelin, *B*, 101–102, 108–113 ; *v.* CHROMATOGRAPHIC ANALYSIS, and, *e.g.* Klein, Handbuch der Pflanzenanalyse, 1933, **4**, 2, Wien, article by H. Winterstein, 1403).

The density (at 31°) of an Al hydroxygel dried in a desiccator was found to be 1·549. On heating, the density steadily increases and ultimately reaches that of a-Al_2O_3 (*q.v.*). J. W. Mellor and A. D. Holdcroft (Trans. Ceram. Soc. 1911, **9**, 94) record the following values :

Temp. °C.	600	700	800	900	1,200
Density at 15°	2·82	2·83	3·39	3·53	3·92

(*cf.* W. Biltz and A. Lemke, Z. anorg. Chem. 1930, **186**, 377).

The gels are insoluble in water, very slightly soluble in excess of ammonia (0·0240 grms. per 100 c.c. in N- NH_4OH), less soluble in ammonium salt solutions, but easily soluble in solutions of $Al_2(SO_4)_3$; easily soluble in methylamine, dimethylamine, and diethylamine, but insoluble or only very slightly soluble in the ordinary organic solvents.

Aluminium hydroxide sols may be prepared by the hydrolysis of Al acetate ; the dialysis of Al acetate, chloride, or nitrate ; by peptising Al hydroxide gel with $AlCl_3$, HCl, or acetic acid ; or by the protracted washing of the freshly precipitated hydroxide gel. In the presence of a small amount of electrolyte, the sols are thixotropic (E. Schalek and A. Szegvari, Kolloid-Z. 1923, **33**, 331). The sol particles carry a positive charge.

The crystalline forms of Al hydroxide (F. Haber, Naturwiss. 1925, **13**, 1008) belong to four types. γ-Al_2O_3,H_2O has been detected in natural bauxite, and is named *böhmite* (J. Böhm, Z. anorg. Chem. 1929, **149**, 205). It can be prepared by heating a mixture of HNO_3 and aqueous $Al(NO_3)_3$ at 320°–360° in the presence of hydrogen at 200–370 atm. for 12–14 hours (W. Ipatiev and B. Muromzev, Ber. 1927, **60** [B], 1980 ; 1930, **63** [B], 2365). It has d^{20} 3·014 (R. Fricke and H. Severin, Z. anorg. Chem. 1932, **205**, 287), and n (weakly double refracting) 1·624±0·003.

a-Al_2O_3 occurs as Diaspore, and it has not been prepared in the laboratory.

$Al_2O_3,3H_2O$ (d^{15}=2·42–2·43) occurs naturally as *gibbsite* and *hydrargillite*, and may be obtained by the slow decomposition of alkali-aluminate solutions. If the precipitation occurs rapidly, a metastable trihydrate, *bayerite a* (d^{20} =2·529), is obtained (R. Fricke, *ibid.* 1928, **175**, 250 ; 1929, **179**, 287), which on shaking for several weeks in aqueous alkali passes into *hydrargillite* through the intermediate *bayerite b.*

Aluminates.—Aluminium hydroxide is amphoteric, and in aq. solution is assumed to ionise in two ways, namely :

$$Al(OH)_3 \rightleftharpoons Al^{\cdot\cdot\cdot}+3OH'$$

(weak base), and

$$Al(OH)_3 \rightleftharpoons H^{\cdot}+H_2AlO_3' \rightleftharpoons H^{\cdot}+H_2O+AlO_2'$$

(weak acid). The salts of the acidic modification form the aluminates $RAlO_2$ or R_3AlO_3 a vast group of compounds the chemistry of which is imperfectly known (*v.* Mellor, V, 284–300 ; Gmelin, System Nr. 35, *B*, Teil 2). Aluminates which are isomorphous with the naturally occurring magnesium meta-aluminate, MgO,Al_2O_3, are called Spinels (Spinelles, Spinells) (*q.v.*). Related aluminates are now prepared by the semage process for cutting as gem stones (*v.* under *Alumina*).

Sodium aluminate, $NaAlO_2$ or Na_3AlO_3, exists in the solution obtained in the alkaline extraction of bauxite, and may be obtained by evaporating the solution, instead of precipitating the Al_2O_3 from it with carbon dioxide according to the usual procedure. It is employed in dyeing (especially for Turkey red) and calico-printing as a mordant, because of its easy hydrolysis to $Al(OH_3)$ and freedom from iron, while the colours are said to be fixed in a very short time and do not require ageing. It is used in hardening gypsum and bricks, as a substitute for Al sulphate in sizing paper, and in the preparation of lake colours, and has recently been strongly recommended as a coagulant in the lime-soda process of water softening, where it has the advantage over Al sulphate of being an alkaline and therefore non-corrosive reagent (J.S.C.I. 1935, **54**, 143–149T).

Barium aluminate, $Ba(AlO_2)_2$, is prepared by fusing a mixture of bauxite, carbon, and heavy spar, extracting with water, and evaporating to crystallisation. It has been used in softening and purifying water, since it yields with sulphates and carbonates the insoluble barium salts, whilst the gelatinous $Al(OH)_3$ precipitated by hydrolysis carries with it other impurities. It has the obvious advantage over many other water softeners that no soluble salts are formed, but its relatively high price has limited its application.

The ammines $Al_2O_3,3H_2O,NH_3$; $Al_2O_3,2H_2O,2{\cdot}5NH_3$; $Al_2O_3,1{\cdot}5H_2O,2{\cdot}5NH_3$; $Al_2O_3,H_2O,2NH_3$; and $Al_2O_3,2H_2O,2{\cdot}5NH_3$ are produced by the action of liquid NH_3 on the various hydroxygels (R. Willstätter and H. Kraut, Ber. 1923, **56** [B], 150 ; 1924 **57** [B], 1089).

Aluminium nitride, AlN.—This compound can be made by the action of nitrogen or ammonia on the metal above 800° (J. Wolf, Z. anorg. Chem. 1913, **83**, 161). It results from the reactions between Al and KCN, KCNS, N_2O, NO, N_2H_4, or certain organic nitrogen compounds, or between Al_2S_3 and N (K. Kaiser, G.P. 346122, 1920). The preparation on the large scale was attempted by the Serpek process, in which aluminium carbide or a mixture of alumina and carbon was heated to a high temperature in a stream of nitrogen : thus,

$$Al_4C_3+2N_2 \rightleftharpoons 4AlN+3C$$

and

$$Al_2O_3+3C+N_2 \rightleftharpoons 2AlN+3CO$$

(G.P. 181991, 181992, 1907 ; 216746, 1909 ; 224628, 1910). Numerous modifications were suggested, *e.g.* the use of catalysts or reducing agents to lower the reaction temperature, or of Fe–Al alloys in place of or in addition to the

Al_4C_3. The ultimate object, to obtain ammonia and alumina by decomposing the nitride with water, made the process very attractive. Unfortunately, the technical difficulties involved in constructing furnaces to operate at the temperatures demanded, above 1,200°, have not been overcome, and the process is still unworkable (*cf.* Ullmann, **1**, 277–281 ; Gmelin, *B*, 137–145).

Pure AlN is a white hexagonally crystalline powder : heat of formation 57·40±0·75 kg.-cal. per mol. (B. Neumann, C. Kröger, and H. Haebler, Z. anorg. Chem. 1932, **204**, 85) ; *d* 3·05–3·25 ; Moh hardness 9. It melts at about 2,000° (J. Wolf, *ibid.* 1914, **87**, 125), and sublimes at about 1,900° with some decomposition.

AlN is unaffected by H, and no reaction was detected with C, B, or Si even at 1,220°. It reacts slowly with P, O, S, and Br at high temperatures, and rapidly with Cl or S_2Cl_2 ; aq. alkalis react slowly, and fused alkalis rapidly according to the equation $AlN+3KOH = K_3AlO_3+NH_3$; aq. acids yield the appropriate ammonium and aluminium salts.

The reaction with water proceeds only slowly even at the boiling-point, because of the deposition of a protective layer of gelatinous Al hydroxide, but is sufficiently rapid for practical purposes in the presence of alkali-aluminates, or when carried out with stirring in autoclaves at 2–4 atm. (F.P. 367124, 415252 ; G.P. 241339, 1910).

Amines have been prepared by leading the vapours of organic compounds over strongly heated AlN.

An *ammine*, AlN,xNH_3, has been described (F. W. Bergstrom, J. Physical Chem. 1928, **32**, 434, 437).

Aluminium nitrite is unknown.

Aluminium nitrate.—The anhydrous salt has not been prepared. Studies of the systems $Al(NO_3)_3$–H_2O and $Al(NO_3)_3$–HNO_3–H_2O reveal $Al(NO_3)_3,9H_2O$, $Al(NO_3)_3,8H_2O$, and $Al(NO_3)_3,6H_2O$ (G. Malquori, Atti R. Accad. Lincei, 1927 [vi], **5**, 892 ; Gazzetta, 1927, **57**, 663 ; 1928, **58**, 782), and a *tetrahydrate* $Al(NO_3)_3,4H_2O$ is obtained by the action of N_2O_5 on the hexahydrate (N. Parravano and G. Malquori, Atti II Cong. Naz. Pura Appl., Palermo, 1926, 1132).

Al nitrate is made on the large scale as an intermediate in the preparation of pure alumina ; by the dissolution of $Al(OH)_3$ in HNO_3; or by the double decomposition of aq. Al sulphate and aq. Pb nitrate or Ca nitrate. In the preparation from Ca nitrate, Al sulphate is dissolved in an approximately equal amount of water by heating with live steam, and is treated with rather less than the theoretical quantity of aq. Ca nitrate (76°Tw.). The clear liquid is filtered from the precipitated Ca sulphate, the excess of sulphate ion precipitated as Ba sulphate with Ba carbonate or aq. Ba nitrate, and the clear filtrate concentrated to 96°Tw., acidified with HNO_3, and crystallised in porcelain or aluminium vessels.

The nitrate obtained in this way contains iron. A completely iron-free product is prepared by dissolving pure $Al(OH)_3$ in iron-free nitric acid. The hydrated alumina is made from the aluminate solution obtained in the alkali extraction process (*q.v.*). Iron is first removed by gradually adding dilute aq. Mg nitrate solution with constant stirring, when it is carried down with the Mg hydroxide precipitate, and as soon as the clear liquid is negative to thiocyanate, the Al hydroxide is precipitated in the usual way with carbon dioxide.

In Norway, labradorite (in Italy, leucite), previously calcined at 500° and finely ground, is dissolved in 30% HNO_3, leaving unattacked most of the iron compounds, the last traces of which may be removed as $Fe(OH)_3$ by the cautious addition of Al hydroxide or Ca carbonate followed by filtration. The nitrate solution is then evaporated, when $KNO_3,Al(NO_3)_3,9H_2O$ deposits, and may be extracted at 20° with 60% HNO_3 in which Al nitrate but not K nitrate is soluble ; or the aqueous solution may be fractionally crystallised from neutral or slightly alkaline solution.

Aluminium nitrate is used as a mordant for textile printing with alizarin red (*q.v.* under *aluminium nitrate-acetate*), and in the manufacture of gas-mantles.

A number of hydrated salts have been prepared. $Al(NO_3)_3, 9H_2O$ is deliquescent, easily soluble in H_2O, $C_2H_5{\cdot}OH$, and liquid NH_3, slightly soluble in acetone, and insoluble in pyridine. On heating, it melts at 73·5°, and passes into $Al(NO_3)_3,6H_2O$. At 140° basic salts are formed, which begin to yield alumina at 200°. $Al(NO_3)_3,8H_2O$ is not deliquescent, is soluble with difficulty in alcohol, and insoluble in ether. $Al(NO_3)_3,4H_2O$ may be heated to 180° without decomposition.

Basic aluminium nitrates are formed by heating $Al(NO_3)_3,9H_2O$, *e.g.* $4Al_2O_3,3N_2O_5,14H_2O$ and $Al_2O_3,2N_2O_5,9H_2O$; by the action of Al on the hot aq. nitrate, *e.g.* $2Al_2O_3,N_2O_5,10H_2O$; and by the action of aq. $NaHCO_3$ on the aq. nitrate, *e.g.* $Al_2O_3,2N_2O_5,H_2O$. A basic salt $Al(OH)_2NO_3,3H_2O$ has been prepared by dissolving Al_2O_3 in ⅓ to ⅔ of the normal quantity of nitric acid (I.G. Farbenind. A.-G., H. Finkelstein, G.P. 444517, 1925).

Aluminium subfluorides are said to have been prepared (W. Hampe, Chem.-Ztg. 1889, **13**, 1, 49, 162, *cf.* W. Diehl, *ibid.* 1889, **13**, 162 ; H. S. Blackmore, J.S.C.I. 1897, **16**, 218), but their existence has not been confirmed.

Aluminium fluoride, AlF_3.—The anhydrous fluoride may be prepared by the reaction between the metal and F at dull red heat, or HF at 1,000° ; by heating dried, calcined $Al(OH)_3$ in HF at 400°–700° (*e.g.* Aluminium Ltd., Canada, F.P. 730427, 1932) ; by fusing cryolite with anhydrous $Al_2(SO_4)_3$; or by heating aluminium ammonium fluoride (W. Biltz and E. Rahlfs, Z. anorg. Chem. 1927, **166**, 370; G. B. Brook and A. C. Coates, B.P. 22088, 1933). $Al_2(SiF_6)_3$ is decomposed at 600° to form AlF_3 and SiF_4. The latter can be combined with HF to give H_2SiF_6, which reacts with Al_2O_3 to form a further supply of $Al_2(SiF_6)_3$ (J. Wilkinson and Son, Ltd., C. J. Saurin, B.P. 421139, 1933). Large quantities are also made by dissolving Al minerals (*e.g.* kaolin, bauxite) in aq. HF. After dissolution, SiO_2 is precipitated by the addition of Al_2O_3, heavy metals and Fe^{III} may be removed with H_2S, and the hydrated Al fluoride crystallised by evaporation, by strong cooling, or by heating in an autoclave. The hydrated fluoride may be dehydrated by calcination (*e.g.* I.G. Farbenind. A.-G., M. Schnetka, G.P. 529602, 1929).

The heat of formation of AlF_3 is +331·5 kg.-cal. per mol. It forms colourless hexagonal rhombohedra ; *d* 2·882–3·22 (W. Biltz and E. Rahlfs, Z. anorg. Chem. 1927, **166**, 374 ; A. Ferrari and A. Sherillo, Gazzetta, 1929, **59**, 930) ; specific heat between 15° and 53° 0·22945. It sublimes without melting at 1,291° and 760 mm. ; heat of sublimation 72·41 kg.-cal.

AlF_3 is insoluble in most solvents. The solubility in water at 25° is 0·559 grms. per 100 c.c. of solution. AlF_3 is inert, being unaffected by aq. acids and bases, and only slowly attacked by fusion with Na_2CO_3.

The *hydrated fluorides* $AlF_3,9H_2O$; $AlF_3,3\frac{1}{2}H_2O(Al_2F_6,7H_2O)$; $AlF_3,3H_2O$; AlF_3,H_2O ; and $AlF_3,\frac{1}{2}H_2O$ have been prepared, of which $AlF_3,3H_2O$ (or perhaps $AlF_3,3\frac{1}{2}H_2O$) is the stable form at the ordinary temperature, while AlF_3,H_2O occurs naturally as *fluellite*. $AlF_3,3H_2O$ and $AlF_3,3\frac{1}{2}H_2O$ each exist in a soluble and an insoluble modification, while $AlF_3,3\frac{1}{2}H_2O$ on heating yields $AlF_3,\frac{1}{2}H_2O$, which is stable at red heat.

Aluminium hydrofluorides.—The compounds $3AlF_3,2HF,5H_2O$ and $2AlF_3,HF,5H_2O$ have been described (H. St.-C. Deville, Ann. Chim. Phys. 1861 [iii], **61**, 329).

Basic aluminium fluorides.—Definite salts are unknown (*see*, however, E. Baud, *ibid.* 1904 [viii], **1**, 62 ; J. J. Berzelius, Pogg. Ann. 1824, **1**, 23).

Ammines of aluminium fluoride.—The compounds AlF_3,NH_3 (G. L. Clark, Amer. J. Sci. 1924 [v], **7**, 7), $AlF_3,2NH_3,2H_2O$, and $AlF_3,NH_3,2H_2O$ (W. Biltz and E. Rahlfs, Z. anorg. Chem. 1927, **166**, 353) have been described.

Double fluorides, etc.—AlF_3 forms numerous complexes with the fluorides of other elements, a number of which occur naturally, *e.g. cryolithionite* $2AlF_3,3NaF,3LiF$ (Greenland, Urals), and *chiolite*, $3AlF_3,5NaF$ (Urals), and may be prepared by fusing the constituent fluorides.

Cryolite, $AlF_3,3NaF$ is the most important of the double fluorides. The only large deposit at present available is mined at Ivigtut (Western Greenland). Recently cryolite of good quality has been prepared, although, through imperfect dehydration, there is a tendency for the artificial material to show greater loss on heating than does the natural mineral.

It has been synthesised by mixing solutions of Na fluoride and Al fluoride (G.P. 35212), when the insoluble double salt precipitates. In another process, Al hydroxide is dissolved in excess of HF, when $AlF_3,3HF$ is formed in solution. On neutralisation with Na_2O_2 insoluble cryolite is precipitated and a salt-free solution of hydrogen peroxide remains. Alternatively, 3 mols. of NaCl may be added directly to the acid solution containing one mol. $AlF_3,3HF$, when pure cryolite precipitates and only requires calcining before use.

From the technical standpoint the chief difficulty rests in avoiding the presence of silicon which finds itself *via* SiF_4 as Na_2SiF_6 in the finished cryolite. The use of the toxic and dangerous HF is also unpleasant. To avoid it, siliceous fluorspar is allowed to react with Na bisulphate :

$$2CaF_2+4NaHSO_4+SiO_2 \\ =SiF_4+2Na_2SO_4+2CaSO_4+2H_2O$$

the volatile SiF_4 is trapped in solid hydrated Na sulphate to form Na silicofluoride, which is melted at 70° with 2 equivalents of sodium carbonate :

$$Na_2SiF_6+4Na_2CO_3+10H_2O \\ =6NaF+SiO_2+4NaHCO_3+8H_2O$$

The silicon is precipitated as SiO_2, and the cryolite obtained by adding aq. Na aluminate :

$$6NaF+4NaHCO_3+NaAlO_2 \\ =Na_3AlF_6+4Na_2CO_3+2H_2O$$

Cryolite, *d* 2·95–3·0, m.p. *circa* 1,000°, hardness 3, is decomposed by hot conc. H_2SO_4 and reacts at higher temperatures with NH_4Cl, some NaCl being formed. In the molten state it is reduced to Al by Na or Mg, and is employed in making enamels and opaque white glass, and as a flux in the manufacture of aluminium. The melting-point of mixtures of cryolite and alumina is said to be :

Cryolite.	1000°.
With 3% Al_2O_3 . . .	974°
,, 6% ,, . . .	960°
,, 10% ,, . . .	980°
,, 15% ,, . . .	994°
,, 20% ,, . . .	1,015°

(Pyne, Trans. Amer. Electrochem. Soc. 1906, **10**, 63 ; Pascal and Jouniaux, Bull. Soc. chim. 1913 [iv], **13**, 439).

Aluminium subchlorides.—The possible existence of a subchloride ($AlCl_2$?) by the action of Cl on an Al–Cu-alloy in vacuum between 400° and 500° has been indicated by L. Frommer and M. Polanyi (Z. physikal. Chem. 1930, B, **6**, 380).

Aluminium chloride, $AlCl_3$.—Anhydrous Al chloride is prepared in the laboratory by passing Cl or HCl over heated Al (G. A. Dawson, J. Amer. Chem. Soc. 1928, **50**, 133 ; K. Bodendorf, J. pr. Chem. 1931 [ii], **129**, 340). It also results from the reactions between Al_2O_3 and Cl, $COCl_2$, CO and Cl, CCl_4, S_2Cl_2, and numerous other chlorides. Large quantities are prepared by heating briquettes of bauxite and carbon in a stream of chlorine (*e.g.* The Chem. Trade J. and Chem. Eng., 19th July, 1929). In the process used by the Texas Gulf Refining Company 3 parts of bauxite previously calcined at 1,000° are mixed with 1 part of coke, milled and briquetted with the addition of asphalt. After drying at 800° the briquettes are transferred immediately to the furnace where they are treated with air for 15 mins., a portion of the carbon being thereby burned and the temperature raised to 870°. Cl is then led through the furnace for 8 to 10 hours and the Al chloride in the effluent gas condensed (A. M. McAfee, Ind. Eng. Chem. 1929, **21**, 670 ; L. M. Aycock, *ibid.* 1930, **22**, 429). In the process used by the I.G. Farbenind. A.-G. (C. Wurster, Z. angew. Chem. 1930, **43**, 877) a mixture of CO and Cl previously passed through a catalyst to form $COCl_2$, is led into the lower end of a vertical furnace containing bauxite which is continuously admitted from the upper end. The spent bauxite residues are removed from the lower end of the furnace, while $AlCl_3$, mixed with CO_2, is led from a side tube situated near the top, and condensed. The products thus prepared are suitable (97% $AlCl_3$) for their major use, the cracking of oils, but where necessary they may be purified by melting in the presence of Fe, Al, or Zn, by passing the vapour through molten Pb, or by treatment with $COCl_2$ and subsequent decomposition of the $COCl_2$–$AlCl_3$ addition compound. Al chloride is only imperfectly purified by sublimation.

The pure anhydrous chloride, heat of formation 167 kg.-cal. per mol., forms colourless or slightly yellow crystals, having a laminated hexagonal lattice of which the unit cell is an hexagonal rhombohedron (W. E. Laschkarev, Z. anorg. Chem. 1930, **193**, 270) ; d_4^{25} 2·44 (W. Biltz and W. Wein, Z. anorg. Chem. 1922, **121**, 260), b.p. 180°–180·2° (W. Fischer and O. Rahlfs, *ibid.* 1932, **205**, 37), m.p. 192·6°/1715 mm., heat of sublimation 27·02–27·41 kg.-cal. per mol. The vapour pressure has been determined by Fischer and Rahlfs (*ibid.* 1932, **205**, 24) and by A. Smits, J. L. Meyering, and M. A. Kamermans (Proc. Acad. Amsterdam, 1932, **35**, 194).

Aluminium chloride in the solid and liquid states consists of Al_2Cl_6 mols. (W. Biltz, Z. anorg. Chem. 1922, **121**, 264 ; Fischer and Rahlfs, *l.c.* ; J. A. M. van Liempt, Rec. trav. chim. 1932, **51**, 1131). At 400° the vapour density corresponds to Al_2Cl_6, at 800° to $AlCl_3$. In solvents with which it combines the mol. is $AlCl_3$; in indifferent solvents, *e.g.* CS_2, it is Al_2Cl_6.

The chloride is deliquescent and 100 grms. of the saturated aq. solution contain 31·36 grms. at 20°, and has d^{25} 1·316.

Al chloride is a stable compound and is only attacked with difficulty by the ordinary reagents. It forms numerous double salts, such as $2AlCl_3,2NH_4Cl$ and $2AlCl_3$,2, 3, or $6NaCl$, combines with many volatile inorganic substances to yield addition compounds, *e.g.* $AlCl_3,NOCl$; $AlCl_3,H_2S$; $AlCl_3,2HCN$; or $AlCl_3,3As$.

The anhydrous salt finds wide application as a catalyst in organic chemistry in reactions involving condensation, dehydration, reduction, polymerisation, and cracking (*see*, *e.g.* G. Kränzlein, "Aluminiumchlorid in der organischen Chemie," 2 Ed., Berlin, 1932). The aq. solutions are employed in carbonising woollen piece goods (R. S. Horsfall and L. G. Lawrie, "The Dyeing of Textile Fibres," London, 1927).

Al chloride crystallises from solution as $AlCl_3,6H_2O$. $AlCl_3,9H_2O$ has been obtained by crystallising below −8°.

Basic aluminium chlorides.—Basic chlorides, the compositions of which vary between wide limits, have been obtained by the action of $Al(OH)_3$, Na_2CO_3, or $NaOH$ on aq. $AlCl_3$ (*see*, *e.g.* W. D. Bancroft, J. Physical Chem. 1914, **18**, 406 ; M. Adolf and W. Pauli, Kolloid.-Z. 1921, **29**, 282 ; and W. D. Treadwell and O. T. Lien, Helv. Chim. Acta, 1931, **14**, 473). A volatile oxychloride may also exist (W. Fischer and R. Gewehr, Z. anorg. Chem. 1932, **209**, 27).

Ammines of aluminium chloride.—The compounds $AlCl_3$,1, 3, 5, 6, 7, 9, and $14NH_3$ have been prepared and investigated (*see*, *e.g.* W. Klemm and E. Tanke, Z. anorg. Chem. 1931, **200**, 344).

Aluminium hypochlorite exists only in a solution which may be prepared by the action of $CaOCl_2$ on aq. $Al_2(SO_4)_3$ or by dissolving Al in aq. $HClO$.

Aluminium chlorate.—When aq. Ba chlorate is mixed with aq. $Al_2(SO_4)_3$, the liquid filtered, and the filtrate evaporated over H_2SO_4, $Al(ClO_3)_3,9H_2O$ is deposited. From warm solutions $Al(ClO_3)_3,6H_2O$ is obtained. Both salts when rapidly heated yield a basic perchlorate, $2Al(ClO_4)_3,Al_2O_3$; slowly heated they explode. The chlorate is used in textile printing in certain discharge styles (E. Knecht and J. B. Fothergill, "The Principles and Practice of Textile Printing," London, 1936).

Aluminium perchlorate.—Solutions of $Al(ClO_4)_3$ prepared by dissolving $Al(OH)_3$ in aq. $HClO_4$ yield under suitable conditions $Al(ClO_4)_3,15H_2O$, $Al(ClO_4)_3,9H_2O$, and $Al(ClO_4)_3,6H_2O$ (m.p. 100°). $Al(ClO_4)_3,15H_2O$ gives $Al(ClO_4)_3,12H_2O$ by careful dehydration.

An acid salt of complex formula, and a basic salt (*q.v.* under *Aluminium chlorate*) have been described.

Aluminium bromide, $AlBr_3$.—The anhydrous salt is prepared by the action of Br vapour on Al at red-heat, by dropping liquid Br on Al turnings, by adding Al powder in small quantities to liquid Br with constant shaking, or by reducing Al_2O_3 by means of C in a current of Br vapour. Purification is effected by melting in the presence of Al, and then fractionally distilling.

Al bromide, heat of formation ($Al + 3Br$liq.) 121 kg.-cal. per mol., forms white hexagonal rhombohedral crystals, with a lattice energy 1234 kg.-cal. per mol. It has m.p. 97·1°–97·5° ; latent heat of fusion 2·7 kg.-cal. mol. ; specific heat between 22° and 70° 0·08912 g.-cal. ; d_4^{18} 3·205 ; coefficient of cubical expansion 283×10^{-6} ; the molten salt has d^{100} 2·64 ; values for the vapour pressure are recorded by W. Fischer and O. Rahlfs (Z. anorg. Chem. 1932, **205**, 24, 26) ; and when extrapolated give a b.p. 255°/760 mm. and yield by calc. a latent heat of vaporisation of 13·9 kg. cal. per mol. at 410° *abs.*

Al bromide in the solid and liquid states is bimolecular (W. Biltz, Z. anorg. Chem. 1922, **121**, 264). At 440° the vapour density corresponds to Al_2Br_6, at higher temperature to $AlBr_3$. In inert solvents there is an equilibrium between Al_2Br_6 and $AlBr_3$. It is very hygroscopic, and easily soluble in H_2O, liquid Br, liquid H_2S, CS_2, CCl_4, $CHCl_3$, C_2H_5Br, $C_2H_4Br_2$, $(C_2H_5)_2O$, C_6H_6, $C_6H_5{\cdot}NO_2$, $C_6H_5{\cdot}CN$, and in many other solvents. Numerous double salts and addition compounds have been prepared, *e.g.* $AlBr_3,H_2S$, $AlBr_3,PH_3$, and $AlBr_3,2C_5H_5N$, and it is applied in the preparation of organic compounds in a fashion similar to the chloride.

$AlBr_3,15H_2O$ is obtained by cooling aq. Al bromide in a $CaCl_2$–ice freezing mixture, while $AlBr_3,6H_2O$ is deposited in transparent crystalline needles or tablets at the ordinary temperature. The hydrates are soluble in alcohol and decompose on heating.

A basic aluminium bromide has been described (H. Gautier and G. Charpy, Compt. rend. 1891, **113**, 599).

Ammines of aluminium bromide.—The compounds $AlBr_3$,1, 3, 5, 6, 7, 9, and $14NH_3$ have been described and investigated (W. Klemm and E. Tanke, Z. anorg. Chem. 1931, **200**, 344 ; Klemm, E. Clausen, and H. Jacobi, *ibid.* 1931, **200**, 369).

Aluminium bromate, $Al(BrO_3)_3,9H_2O$, m.p. 62·3°, is prepared by evaporating over H_2SO_4 the aq. solution resulting from a solution of $Al(OH)_3$ in aq. $HBrO_3$, or from the reaction between aq. $Ba(BrO_3)_2$ and aq. $Al_2(SO_4)_3$.

Aluminium iodide, AlI_3.—The anhydrous iodide is prepared by allowing Al to react with I dissolved in CS_2, by passing I vapour over heated Al, or by heating to 220° a mixture of iodine (20 grms.) and fine Al filings (2 grms.) in a sealed tube. Purification is effected by melting the impure iodide with metallic Al, and fractionally subliming.

Al iodide, heat of formation (Al+3I solid) 71 kg.-cal. per mol., forms colourless or very pale yellow crystals ; m.p. 191° (corr.) ; latent heat of fusion 3·8 kg.-cal. per mol. ; b.p. 381°–382°/760 mm., d_4^{25} 3·98 ; coefficient of cubical expansion between 20° and 100°, 182×10^{-6}. Values for the vapour pressure are recorded by W. Fischer and O. Rahlfs (Z. anorg. Chem. 1932, **205**, 25) ; latent heat of vaporisation 16·0 kg.-cal. per mol. Al_2I_6, 19·0 kg.-cal. per mol. AlI_3.

The iodide is bimolecular in the liquid and solid states and in solution, but unlike the chloride and bromide is already 24% dissociated to simple molecules at its boiling-point, and the vapour burns in air if ignited.

It is strongly hygroscopic, and very soluble in H_2O, liquid NH_3, liquid H_2S, CS_2, and absolute alcohol, and is soluble in benzol and pyridine. The compounds $AlI_3,2H_2S$, $AlI_3,4H_2S$, and AlI_3,PH_3, numerous double salts of the type AlI_3,KI, and a few complexes with organic molecules have been prepared.

$AlI_3,15H_2O$, m.p. −18° *circa*, is obtained by cooling in $CaCl_2$–ice and $AlI_3,6H_2O$ by evaporating in a vacuum, aq. solutions of Al iodide which may be prepared by dissolving $Al(OH)_3$ in HI, by warming Al and I in the presence of H_2O, or by dissolving the anhydrous Al iodide in water.

Ammines of aluminium iodide.—The compounds AlI_3,1, 3, 5, 6, 7, 9, 13, and $20NH_3$ have been isolated and investigated (W. Klemm and E. Tanke, Z. anorg. Chem. 1931, **200**, 344 ; W. Klemm, E. Clausen, and H. Jacobi, *ibid.* 1931, **200**, 369).

KNH_2 reacts with AlI_3 dissolved in liquid NH_3 to form *ammonobasic derivatives, e.g.* $Al(NH_2)_3$, $AlI_3,6NH_3$ (E. C. Franklin, J. Amer. Chem. Soc. 1915, **37**, 849 ; 1905, **27**, 849).

Aluminium iodate, $Al(IO_3)_3,6H_2O$, and periodate, $Al(IO_4)_3,3H_2O$, have been prepared.

Aluminium and sulphur.—Some unconvincing evidence has been adduced of the existence of *aluminium sub-sulphide*, AlS (F. Regelsberger, Z. Elektrochem. 1897–98, **4**, 548 ; *cf.* W. Biltz, Z. anorg. Chem. 1925, **146**, 289 ; W. Biltz and F. Caspari, *ibid.* 1911, **71**, 195).

Aluminium sulphide, Al_2S_3, has not been prepared in the pure state. A relatively pure specimen has been made by heating an Al–Sb alloy with twice the theoretical amount of Sb_2S_3 in a graphite boat in a hydrogen stream. The product, after heating to 1,000° for 4 hours in a vacuum to volatilise any Sb and Sb_2S_3, contains no oxide and only traces of free Al (Picon, Bull. Soc. chim. 1929 [iv], **45**, 909 ; Compt. rend. 1929, **189**, 97). It is also obtained by melting Al granules with S, and firing the mixture as in a thermite reaction (occasionally attended by explosion) ; by leading H_2S over Al granules at red heat ; by heating Al_2O_3 in CS_2 vapour ; by reducing the sulphate in presence of metallic sulphides ; and it occurs as an intermediate product in a number of the commercial processes used for extracting Al_2O_3, *e.g.* the Haglund Process (*q.v.*).

Al sulphide is a yellowish amorphous or crystalline mass ; heat of formation ($2Al+3S_{solid}$) 126·4 kg.-cal. per mol. ; *d* 2·37. It sublimes in a vacuum at high temperatures with slight dissociation, is hydrolysed by water, reacts rapidly with siliceous materials to yield SiS_2 (W. Biltz, Z. anorg. Chem. 1925, **146**, 289), and with aliphatic compounds above 300° to introduce sulphur and remove hydrogen, while aromatic compounds are in general little affected but may be dehydrogenated (G. R. Levi and H. Nalta, Atti R. Accad. Lincei, 1924 [v], **33**, 350 ; Gazzetta, 1924, **54**, 973). Double salts of the type $Al_2S_3,3NaS$ or Al_2S_3,MgS have been prepared. Al sulphide has been suggested as a fused electrolyte for use in the preparation of aluminium.

Aluminium sulphite, $Al_2(SO_3)_3$, *d* 1·122, is obtained by strongly cooling and constantly shaking a neutral solution of $Al(OH)_3$ in aq. SO_2. An aq. solution is obtained by mixing $Al_2(SO_4)_3,18H_2O$ and $Na_2SO_3,7H_2O$ in a little boiling water, and filtering cold from the precipitated Na sulphate.

The *basic sulphites*, $Al_2O_3,SO_2,4H_2O$, $4Al_2O_3,3SO_2,18H_2O$, and $5Al_2O_3,3SO_2,15H_2O$ have been described.

Aluminium sulphate, $Al_2(SO_4)_3,18H_2O$.—Aluminium sulphate occurs naturally in considerable quantities. As the hydrated salt of the above composition, it forms the chief constituent of the mineral *alunogen*, *halotrichite*, *feather alum*, or *hair salt*, which is found in volcanic districts, at Bilin in Bohemia, Copiapo in Chile, etc. It also occurs in pyritic shale. A sample of feather alum from Friesdorf, Bonn, was found by Roso to contain Al_2O_3 14·9%, SO_3 37·4%, FeO 2·5%, H_2O 45·2%, with traces of K, Na, Mg, and SiO_2.

Aluminite or *websterite*, a hydrated basic salt of the composition $Al_2O_3SO_3,9H_2O$, has been found at Auteuil, Halle, Mulhausen, etc.

In combination with potassium sulphate, the basic salt occurs also in the mineral *alunite*, *alumstone*, or *alum rock* (*q.v.*).

Aluminium sulphate is by far the most important of all the salts of aluminium from the point of view of industrial use, the production in Great Britain being in the neighbourhood of 90,000 tons per annum. It is employed chiefly in the paper industry, where it is used for the fixing of the size which is added to the pulp immediately before going to the paper-making machine, and as a coagulating and precipitating agent in the treatment of sewage and the purification of drinking water. It is usually supplied in solid form, at the maximum crystallising strength of 17–18% Al_2O_3 for paper making, and in the strength of 14–15% Al_2O_3 for water purification.

Aluminium sulphate may be produced by dissolving the metal, the hydrated oxide, or the silicate in sulphuric acid. Of the raw materials available for its manufacture, the two which are of the greatest importance are china clay (kaolin) and bauxite.

The manufacture of aluminium sulphate from china clay has been carried out on an extensive scale by a process based upon the original patent of Pochin, B.P. 231 of 1855. The clay, containing about 40% alumina, is obtained from Cornwall and is selected as free as possible from grit and oxide of iron. It is reduced by milling and sifting to the finest possible state of division and, after a preliminary drying, is calcined at a dull-red heat in a reverberatory furnace. During the calcination the clay suffers a loss in weight amounting to from 20 to 25%, due to the expulsion of the whole of the moisture present (10 to 15%) and of the greater part of the water of hydration. The calcined clay is transferred to a lead-lined wooden vat containing the requisite quantity of sulphuric acid, heated to a temperature of 85° and having a strength at this temperature of 96°Tw. A vigorous reaction immediately takes place, and after the lapse of 15 minutes, during which the contents of the vat are kept well agitated, the product is run into lead-lined wooden waggons in which the reaction continues for a considerable time and the pasty mass gradually solidifies. Finally the solid block is brought under a heavy mechanical knife, and by a combined cutting and crushing action is reduced to the state of a coarse powder.

The product was marketed under the name of "alum cake," and contains the whole of the silica, iron, and other impurities present in the clay, its average composition being: Al_2O_3 (soluble) 12·25 to 13·0%; Fe_2O_3 0·12 to 0·22%; combined SO_3 29·5 to 31·8%, free SO_3 0·4 to 1·0%; insoluble matter 20·0 to 26·5%.

The term "Alum cake" is still applied by some of the older hands, particularly in the paper trade, to the purer forms of sulphate now used, but it is rapidly becoming obsolete in favour of the latter more correct term.

There are two main grades of sulphate of alumina produced to-day, the iron-free grade produced from pure hydrate of alumina and known as pure or white sulphate, and the ferrous grade produced from low-iron bauxite, shale or similar ore and marketed, for water purification purposes, under the trade names of *Alumino-ferric* or *Super-Alumina*. Originally, alumino-ferric was produced from ores with higher percentages of iron than are now used, as the presence of small amounts of iron was not objected to for water purification, but this second-grade sulphate is now available with iron as low as 0·5% and in the ferrous state, which is less marked in colour, with the result that the ferrous grade competes with the pure grade for certain qualities of paper where whiteness is not required. In countries where no supplies of pure hydrate of alumina (a by-product of the aluminium industry), are available the ferrous grade is still further purified from iron by chemical or electro-chemical methods, and an almost iron-free material, with about 0·1% Fe_2O_3 as against about 0·003% for sulphate produced from hydrate of alumina, is obtained.

Pure sulphate of alumina is produced commercially by slowly adding pure moist hydrate of alumina, *ex* Bayer Process and containing about 60% Al_2O_3, to boiling iron-free sulphuric acid of about 60°–70°Tw. contained in a lead-lined circular digester, the requisite heat being maintained by means of steam coils. The whole of the hydrate is converted into sulphate and the clear liquid boiled until the required density is attained, after which it is run into tiled crystallising troughs into which lead partitions are inserted before crystallisation is complete. This material, containing 17–18% Al_2O_3, is usually supplied either kibbled or powdered, packed in bags, and ready for dissolving in the paper pulp.

Ferrous sulphate of alumina is produced in a similar manner, using low-iron bauxite containing about 60% Al_2O_3, shale, or similar ore which has, in some cases, to be treated to convert the iron from the ferric to the ferrous condition. The bulk of the alumina contained in the ore is converted to sulphate and the whole contents of the digester are then run to settling tanks for removal of the solid residues, mostly silica, after which the clear liquor is evaporated until the desired strength is attained, when it is run into troughs made of glazed bricks and treated in the same manner as the pure sulphate. Some makers add other materials towards the finish of the digesting stage to reduce the excess acidity and complete the conversion of the iron to the ferrous state, but the nature of these operations is kept secret. This material, containing 14–15% Al_2O_3, is usually supplied in slab or broken form for ease of transport.

In addition to these two main grades, intermediate grades are also produced or supplied, in accordance with local conditions. For sewage precipitation a *ferric-alumina*, produced from bauxite residue and containing more iron sulphate than aluminium sulphate, is also coming into use. As the Al_2O_3 content of this material is below the crystallisation point at any strength, it is supplied in the liquid form or made on site by the sewage works.

The anhydrous salt is obtained by heating the hydrates at 250°–450° (L. Hackspill and A. P. Kieffer, Ann. Chim. 1930 [x], **14**, 273). It has a heat of formation ($2Al,3S,12O+aq.=Al_2(SO_4)_3$ diss.) of 879·7 kg.-cal. per mol.; d^{17} 2·71, $d^{22\cdot5}$ 2·672; specific heat 0·1855 g.-cal.; and a mean refractive index of 1·47.

Anhydrous $Al_2(SO_4)_3$ is completely decomposed at 750° into Al_2O_3 with the evolution of SO_2 and SO_3. The system $Al_2(SO_4)_3–H_2O$ reveals only one hydrate, $Al_2(SO_4)_3,18H_2O$, d^{17} 1·691, but $Al_2(SO_4)_3,16H_2O$ appears in the system $Al_2(SO_4)_3–Al(OH)_3–H_2O$. Fractional dehydration of fully hydrated Al sulphate indicates the existence of $Al_2(SO_4)_3$ with 27, 18, 16, 10, or $6H_2O$ (K. Krauss and A. Fricke, Z. anorg. Chem. 1927, **166**, 174). In addition, $Al_2(SO_4)_3$ with 13, 12, 9, 7, 4, 2, or $1H_2O$ has been prepared. The solubility in water and the density of aqueous solutions of Al sulphate are recorded in the following tables:

Temp. °C.	Solubility in 100 parts of water.	
	$Al_2(SO_4)_3$.	$Al_2(SO_4)_3,18H_2O$.
0	31·3	86·8
10	33·5	95·8
20	36·1	107·3
30	40·4	127·6
40	45·7	167·6
50	52·1	201·4
60	59·1	262·6
70	66·2	348·2
80	73·1	467·3
90	80·8	678·8
100	89·1	1132·0

(Poggiale, Ann. Chim. Phys. 1843 [iii], **8**, 467).

DENSITY OF AQUEOUS ALUMINIUM SULPHATE SOLUTIONS.

Percentage $Al_2(SO_4)_3$.	Density at 15°C.	Percentage $Al_2(SO_4)_3$.	Density at 15°C.
1	1·017	14	1·1467
2	1·027	15	1·1574
3	1·037	16	1·1668
4	1·047	17	1·1770
5	1·0569	18	1·1876
6	1·0670	19	1·1971
7	1·0768	20	1·2074
8	1·0870	21	1·2168
9	1·0968	22	1·2274
10	1·1071	23	1·2375
11	1·1171	24	1·2473
12	1·1270	25	1·2572
13	1·1369		

Percentage $Al_2(SO_4)_3$.	Density at 25°C.	Density at 35°C.	Density at 45°C.
5	1·0503	1·0450	1·0356
10	1·1022	1·0960	1·0850
15	1·1522	1·1460	1·1346
20	1·2004	1·1920	1·1801
25	1·2483	1·2407	1·2295

(K. Reuss, Ber. 1884, **17**, 2890).

The viscosities of the aqueous solutions are as follows:

Conc. in mol. litre.	0·0490	0·0980	0·1960	0·3655
$\eta\times10^5$ at 15°	1270	1410	1778	2768
$\eta\times10^5$ at 35°	792	873	1064	1621
$\eta\times10^5$ at 55°	—	598	714	1007

(M. Bobtelsky and Malkova-Janovskaja, Z. anorg. Chem. 1927, **165**, 250).

Anhydrous Al sulphate is insoluble in ethyl acetate, very slightly soluble in $CH_3{\cdot}OH$ and $C_2H_5{\cdot}OH$ (0·018 grms. per 100 c.c. solution at 20°), and gives a 14·4% solution in glycol.

The sulphate is the most important and widely applied of aluminium compounds. Besides its use in the preparation of alums (*q.v.*), it is employed in water purification, tanning, paper-making, in the water-proofing of cloth, and in the preparation of mordants (R. S. Horsfall and L. G. Lawrie, "The Dyeing of Textile Fibres," Benn, London. 1927). The amounts produced and used in various industries have been recorded by F. J. Curtis (Chem. Met. Eng. 1926, **33**, 687) and C. L. Mantell (Min. Ind. 1931, **39**, 27).

Acid aluminium sulphates, $Al_2(SO_4)_3,3H_2SO_4,7H_2O$; $Al_2(SO_4)_3,2H_2SO_4,10H_2O$; and $Al_2(SO_4)_3,H_2SO_4,3H_2O$ have been obtained by crystallising solutions of Al sulphate in aq. H_2SO_4, while $Al_2(SO_4)_3,H_2SO_4,14H_2O$ occurs in lead-chamber sludge.

Basic aluminium sulphates.—Basic salts of indefinite composition have been prepared by precipitating Al sulphate solutions with caustic alkalis, ammonia, or chalk (*see, e.g.* W. D. Bancroft, J. Physical Chem. 1914, **18**, 401, 407; F. S. Williams, *ibid.* 1923, **27**, 284; S. V. Pickering, Chem. News, 1882, **45**, 121, 133, 146). Only one such compound appears in the system $Al_2(SO_4)–Al(OH)_3–H_2O$. It is crystalline, and has the composition $Al_2O_3,2SO_3,12H_2O$, identical with that of the mineral *Alumian* which occurs in southern Spain, and may be made by adding lime or the calc. amount of $Al(OH)_3$ to aq. $Al_2(SO_4)_3$.

Basic aluminium sulphate is produced commercially by precipitating the bulk of the alumina in a highly dispersed form from a weak solution of pure acid sulphate by means of soda and repeated washings to eliminate the sodium sulphate formed. It is subsequently filter-pressed and carefully dried. It is marketed either as *Alumina Hydrate*, *Soluble Alumina*, *Alumina White*, or under various other trade names, it contains about 50% of Al_2O_3 and less than 10% of SO_3, and is used as a mordant in the colour and printing ink trades.

Aluminium dithionate, $Al_2(S_2O_6)_3,18H_2O$, is obtained by dissolving $Al(OH)_3$ in dithionic acid, or by adding BaS_2O_6 to aq. $Al_2(SO_4)_3$. It forms colourless, very deliquescent tablets, which dissolve at 60° in their water of crystallisation and begin to decompose.

Aluminium chlorosulphate,

$$AlSO_4Cl,6H_2O,$$

is obtained by passing HCl gas into impure aq. $Al_2(SO_4)_3$ (V. Gerber, Z. Elektrochem. 1919, **25**, 199).

Aluminium selenide, Al_2Se_3, is obtained by the strongly exothermic and often explosive reaction between the elements. It is best prepared by a thermite reaction, or by dropping, a little at a time, a mixture of the elements containing slightly more than the theoretical quantity of selenium into a heated round-bottomed Pyrex glass flask (*see also* L. Moser and E. Doctor, Z. anorg. Chem. 1921, **118**, 286).

It forms a light-brown friable mass, which reacts rapidly with water and with aq. mineral acids to give H_2Se, and attacks many organic compounds with the evolution of H_2Se and formation of seleno-mercaptans and selenides.

Aluminium selenite, $Al_2(SeO_3)_3,7H_2O$, is obtained as insoluble prismatic crystals by treating the basic selenite $4Al_2O_3,9SeO_2,36H_2O$, which is precipitated by the action of aq. Na_2SeO_3 on aq. Al salt solutions, with aq. SeO_2. The heptahydrate yields a trihydrate $Al_2(SeO_3)_3,3H_2O$ when heated to 230° in a sealed tube with dilute aq. SeO_2.

In addition to the *basic selenite* already mentioned, several *acid selenites* have been prepared, *e.g.* $Al_2O_3,6SeO_2$; $Al_2O_3,6SeO_2,2H_2O$; $Al_2O_3,6SeO_2,5H_2O$ (*see, e.g.*, V. Lenher and E. J. Wechter, J. Amer. Chem. Soc. 1925, **47**, 1523).

Aluminium selenate, $Al_2(SeO_4)_3,18(\text{or }16)H_2O$ is made by strongly cooling a solution of $Al(OH)_3$ in H_2SeO_4. The selenate is very soluble in water, less so in the presence of alcohol or glacial acetic acid.

Aluminium telluride, Al_2Te_3, may be made in a similar way to the selenide. A purer product has been obtained by allowing Te vapour to react with Al in a vacuum at red heat (L. Moser and K. Ertl, Z. anorg. Chem. 1921, **118**, 271). Al telluride is a dark brown, glistening, amorphous mass, rapidly hydrolysed by water and acids yielding H_2Te and much elementary tellurium. It reacts, but only with difficulty, with organic compounds (*cf.* aluminium selenide).

A stable compound Al_5Te appears in the system Al–Te (M. Chikashige and J. Nosé, Mem. Sci. Kyoto Univ. 1916–1917, **2**, 227).

Aluminium tellurite and *aluminium tellurate* have been described as insoluble, flocculent precipitates (J. J. Berzelius, Pogg. Ann. 1834, **32**, 594 ; Ann. Chim. Phys. 1835 [ii], **58**, 244, 259).

Aluminium silicates (*v.* SILICATES). These compounds are exceedingly numerous and important. As an anhydrous silicate, with silicate of iron, calcium, magnesium, etc., aluminium occurs in the varieties of *garnet*, crystallising in the regular system. As silicate of aluminium, calcium and sodium it is found in *lapis-lazuli*, which was formerly used as *ultramarine*. It is now replaced by artificial ultramarine (*v.* ULTRAMARINE). As silicate of aluminium, combined with potassium, iron and magnesium, it occurs in the *micas*. As double silicate of aluminium, potassium, sodium, magnesium or calcium, it forms the varieties of *felspar* which occur in immense quantities in eruptive rocks. By the decomposition of felspar by the carbonic acid in the atmosphere and in rain or spring water, the alkaline compounds are removed, leaving kaolin or clay of more or less purity (*v.* CLAY), which, under pressure, becomes hardened and laminated forming *shale*, and finally *slate* (*q.v.*). Many of the silicates of aluminium are of great importance and of wide application, and are prepared in large quantities artificially, *e.g.* Zeolites (*v.* PERMUTITE). The more important of them are considered under their applications (*v.*, *e.g.*, CERAMICS, POTTERY, PORCELAIN).

Aluminium and boron.—The reaction between aluminium and boron or boron compounds yields either AlB_2 or AlB_{12} (H. Funk, Z. anorg. Chem. 1925, **142**, 274 ; H. Biltz, Ber. 1910, **43**, 306). The former is stable below 1,500° but gives place to the latter, in the presence of a sufficiency of boron, at higher temperatures. AlB_2 consists of bronze-coloured needles or tablets, slowly attacked at high temperatures by O, slowly soluble in concentrated aq. acids and alkalis with the evolution of hydrogen, and inflaming in Cl to yield $AlCl_3$ and BCl_3.

AlB_{12} forms reddish-black monoclinic crystals, d_4^{18} 2·554±0·005, harder than corundum but somewhat softer than diamond, and very resistant to chemical attack.

Aluminium borates.—Al_2O_3,B_2O_3 is precipitated by adding $Al(OH)_3$ to a hot saturated boric acid solution, and $3Al_2O_3,B_2O_3$ by melting the constituent oxides. Basic precipitates of complex formula are obtained by the reaction between Al salt solutions and aq. $NaBO_2$ or $Na_2B_4O_7$.

Aluminium carbide, Al_4C_3, has been suggested as a refractory, corrosion-resisting material and as a starting point in the manufacture of metallic aluminium. For these purposes, it has been made by strongly heating briquettes of bauxite and carbon. In the laboratory it is prepared by gradually heating a mixture of Al and C in theoretical proportions in an electric furnace to 2,000° (O. Ruff and E. Jellinek, Z. anorg. Chem. 1916, **97**, 316). It is also obtained by heating Al in a stream of CO, CH_4, or C_2H_2.

Al carbide, heat of formation 111·2 kg.-cal. per mol, *d* 2·36, m.p. >2,200° (decomp.), forms transparent hexagonal yellow crystals, an amorphous black powder or a fused mass. It is slowly decomposed by water, and more quickly by dilute acids and alkalis forming methane, but is only slowly affected by concentrated mineral acids. O, Cl, and Br, but not I, attack it at red heat. Pring (J.C.S. 1905, **87**, 1530) found that up to 1,400°C. the carbide acts as a reducing agent on metallic oxides :

$$Al_4C_3+12MO=2Al_2O_3+3CO_2+12M$$

but at higher temperatures alloys of aluminium and the metal are produced:

$$Al_4C_3+3CuO=Al_4Cu_3+3CO$$

owing to the fact that alumina can be reduced by carbon at very high temperatures ; at lower temperatures the aluminium is oxidised by carbonic oxide as observed by Moissan:

$$6Al+3CO=Al_4C_3+Al_2O_3$$

Lower carbides, Al_3C_2 and AlC_3 may exist, but their individuality is dubious (O. Ruff and E. Jellinek, Z. anorg. Chem. 1915, **97**, 322 ; J. F. Durand, Bull. Soc. chim. 1924 [iv], **35**, 1143 ; S. Peacock, E.P. 11394, 1912).

Aluminium carbonyl.—A substance which may be $Al_4(CO)_3$ (R. Brunner, Z. Elektrochem. 1932, **38**, 68), and an *iodo-chlorocarbonyl*, $Al_3(CO)_2Cl_2I$ (A. v. Bartal, Z. anorg. Chem. 1908, **56**, 50), have been prepared.

Aluminium carbonate.—The normal carbonate is unknown, but numerous *basic carbonates* have been obtained by precipitating Al salt solutions with alkali carbonates, *e.g.* $Al_2O_3,CO_2,2H_2O$; $3Al_2O_3,2CO_2,16H_2O$. Their effect in the photosynthesis of organic compounds is discussed by E. C. C. Baly *et alia* (Proc. Roy. Soc. 1927, A, **116**, 205).

Aluminium borocarbide, $Al_3C_2B_{44}$, d_4^{18} 2·590 ± 0·006, forms yellow crystals a little softer than diamond (W. Hampe, Annalen, 1876, **183**, 90 ; H. Biltz, Ber. 1910, **43**, 299).

Aluminium cyanide, $Al(CN)_3$, exists only in solution in water, or in liquid ammonia. The latter is obtained by allowing Al to react with $Hg(CN)_2$ in liquid NH_3 solution (F. W. Bergstrom, J. Amer. Chem. Soc. 1924, **46**, 1559). From the solution the *ammines* $Al(CN)_3$, 14 (or 13), 9, 6, and $5NH_3$, are deposited under different conditions of crystallisation, while $Al(CN)_3,5NH_3$ heated to 80° in a vacuum yields $Al(CN)_3,1{\cdot}5NH_3$.

Aluminium cyanamide has been prepared by the action of gaseous HCN on Al oxide (H. H. Franck and H. Heimann, Z. angew. Chem. 1931, **44**, 377).

Aluminium thiocyanate (sulphocyanide), $Al(CNS)_3$, is employed as a mordant in place of the acetate for alizarin, steam reds, etc. ; the colours produced are said to be especially permanent, as undesirable traces of iron in the thiocyanate are revealed by the blood-red colour due to ferric thiocyanate. Lauber and Haussmann (Dingl. poly. J. 1882, **245**, 306) recommend the following method of preparation: 5 kilos aluminium sulphate are dissolved in 5 litres boiling water, 250 g. of chalk are added, followed by 11·5 litres of crude calcium thiocyanate solution of 30°Tw., and the whole well stirred and allowed to settle. The clear liquid is ready for use. The solutions assume a red colour when exposed to sunlight, but become colourless again in the dark; they may be evaporated to a syrupy consistency without decomposition, but only *basic thiocyanates* can be recovered from them (W. Liechti and W. Suida, *ibid.* 1884, **251**, 183 ; W. D. Bancroft, J Physical Chem. 1914, **18**, 406).

An *ammine* $Al(CNS)_3,5NH_3$ is formed when sulphur reacts with $Al(CN)_3$ dissolved in liquid NH_3 (F. W. Bergstrom, J. Amer. Chem. Soc. 1926, **48**, 2322), and the double compounds $Al(CNS)_3,(C_2H_5)_2O$ and $[Al(COC_{10}H_{12}N_2)_6](CNS)_3$, m.p. 103°–105°, are obtained with ether and antipyrine respectively.

Aluminium selenocyanate exists only as the *ammine*, $Al(CNSe)_3,5NH_3$ (F. W. Bergstrom, *l.c.*, 2324).

ALUMINIUM, ORGANIC COMPOUND OF.

Aluminium formate, $Al(HCO_2)_3$, and *basic formate*, $Al(OH)(HCO_2)_2$, are prepared by the evaporation of solutions of $Al(OH)_3$ in formic acid. The aqueous solutions employed in textile printing, tanning and as antiseptics in pharmacy are generally made by the addition of aq. Na or Ca formate to aq. Al sulphate, or alum.

Aluminium chloro-formate, $Al(HCO_2)_2Cl,H_2CO_2,2\frac{1}{2}H_2O$ (*see* A. Benrath, J. pr. Chem. 1905 [ii], **72**, 232).

Aluminium acetate, $Al(CH_3{\cdot}CO_2)_3$, may be prepared in solution by dissolving $Al(OH)_3$ in acetic acid, or by the double decomposition of Al sulphate with Pb or Ba acetate. In a very pure state for pharmaceutical work it is made by the anodic dissolution of Al in acetic acid The existence of normal Al acetate is questionable, but several well-defined *basic salts* have been obtained in the laboratory and on the technical scale from the aq. solutions, *e.g.* $Al(OH)(CH_3{\cdot}CO_2)_2$; $Al_2O(CH_3{\cdot}CO_2)_4$; $Al_2(OH)_3(CH_3{\cdot}CO_2)_3$; and $Al(CH_3{\cdot}CO_2)_3,2AlO(CH_3{\cdot}CO_2)$. The basic salts tend to contain besides, variable amounts of combined or adsorbed sulphate, nitrate, or halide from the salts used in their preparation.

The constitution of the aqueous solutions has been only superficially investigated, but by analogy with solutions of ferric acetate, they are probably complex, and in view of their easy hydrolysis almost always contain variable amounts of Al_2O_3-sol (*q.v.*).

Numerous double salts with organic acids and carbohydrates have been described.

The acetate finds wide application in sizing paper, hardening cardboard, as an accelerator in tanning, in the proofing of fabrics and paper and as an antiseptic and astringent.

Aluminium sulphate-acetate, red liquor, is an aqueous solution of Al sulphate and Al acetate much used as a mordant for dyeing with alizarin reds and Turkey red (R. S. Horsfall and L. G. Lawrie, "The Dyeing of Textile Fibres," Benn, London, 1927 ; "Acetate Silk and Its Dyes," C. E. Mullin, Constable, 1928 ; Knecht and Fothergill, "The Principle and Practice of Textile Printing," London, 1936). The *normal sulphate-acetate* may be prepared by dissolving 6,650 g. Al sulphate in 6 litres of water, and adding to 9,450 g. of sugar of lead dissolved in 9 litres of hot water, filtering and diluting to 15°Tw. The *basic* sulphate-acetate is made by dissolving 1,908 g. of alum or 1,330 g. of Al sulphate in 2 litres of water, and adding to 1,590 g. of sugar of lead in 1,600 c.c. of hot water. After precipitating and cooling, 150 g. Na carbonate crystals are added, the mixture allowed to stand 12 hours, the clear liquor removed and diluted to 18°Tw.

Aluminium nitrate-acetate is used for giving a fiery tone to alizarin oranges and scarlets, and is made by dissolving separately and subsequently mixing 10½ lb. Al sulphate, 2¼ lb. acetate of lime, and 6¾ lb. nitrate of lime. This solution, to which ¼ oz. of K ferrocyanide and ¾ oz. of stannic chloride (53°Tw.) are added to precipitate the iron, is made up to 5 gallons, filtered, and diluted to 8–15°Tw. (Horsfall and Lawrie, *l.c.*, 365).

Aluminium acetylacetonate,

$$Al[(CH_3 \cdot CO)_2CH]_3,$$

prepared by the reaction between anhydrous $AlCl_3$ and acetylacetone in the presence of chloroform (G. T. Morgan and H. D. K. Drew, J.C.S. 1921, **119**, 1060), forms colourless plates, *d* 1·27, m.p. 191°–194°, b.p. 314°–315°. It is insoluble in water, easily soluble in benzene, chloroform and absolute alcohol and less so in ether.

Aluminium citrate, $Al_2(C_6O_7H_5)_2$, is used sparingly in the production of alizarin pinks, and is made by dissolving $Al(OH)_3$ in citric acid.

Aluminium alkyls,[1] AlR_3, are formed by heating on the water bath the appropriate mercury dialkyl with aluminium in a sealed tube. $Al(CH_3)_3$ is a fuming liquid, b.p. 127°–129°, spontaneously inflammable in air, and rapidly decomposed by water. $Al(C_2H_5)_3$, b.p. 194° ; Al tripropyl, b.p. 248°–252° ; Al tri-*iso*butyl ; and Al tri-*iso*amyl, b.p. 250°/80–100 mm., have been described.

The alkyls form etherates with diethyl ether : $4Al(CH_3)_3,3(C_2H_5)_2O$, b.p. 68°/15 mm. ; Al triethyl etherate, b.p. 110·5°/13·5 mm., $d^{17 \cdot 4}$ 0·8200 ; and Al tripropyl etherate, b.p. 135°/18 mm. They are mobile liquids which decompose rapidly in air or water (Krause and Wendt, Ber. 1923, **56** [*B*], 466).

Aluminium alkyl halides are obtained when Al powder reacts, *e.g.* with dry ethyl iodide : $Al(C_2H_5)_2I$, b.p. 118°–120°/4–5 mm., d^{27} 1·609 ; $AlC_2H_5I_2$, m.p. 35°–37°, b.p. 158°–160°/4 mm. (Grignard and Jenkins, Bull. Soc. chim. 1925 [iv], **37**, 1376).

Aluminium triphenyl, $Al(C_6H_5)_3$, m.p. 196°–200°, is formed in the reaction between mercury diphenyl and aluminium. It forms an etherate, $Al(C_6H_5)_3,(C_2H_5)_2O$, m.p. 112°–113°, which decomposes slowly in air, and inflames with water (Hilpert and Grüttner, Ber. 1912, **45**, 2828).

Aluminium ethoxide is prepared by treating anhydrous alcohol with aluminium in presence of a small quantity of mercuric chloride (as a catalyst) and iodine or alkyl halide. The mixture is distilled under reduced pressure when a distillate free from mercury is obtained (Farbwerke vorm. Meister Lucius and Brüning, G.P. 286596 ; J.S.C.I. 1915, **34**, 1168).

Aluminium oxalate, $Al_2(C_2O_4)_3,xH_2O$, is obtained by crystallising the aq. solution obtained by dissolving $Al(OH)_3$ or amalgamated Al in aq. $H_2C_2O_4$. *Di-* and *tetrahydrates* have been identified. Hot, concentrated solutions of the alkali oxalates dissolve $Al(OH)_3$ and deposit complex salts $M_3Al(C_2O_4)_3,xH_2O$.

A number of *acid* and *basic oxalates* have been prepared, the former, however, only as alcoholates.

Aluminium oleate is a soft, white, putty-like substance, of great tenacity, insoluble in water, soluble in ether and petroleum. A mixture of oleate, palmitate and other fatty salts is produced from whale, cotton-seed and similar oils by saponification with soda and addition of the sodium salt so produced to a solution of alum. The gummy precipitate is known as "oil pulp," and is dissolved in 4 or 5 parts of mineral oil to form a "thickener" for addition to the lubricator. A sample of oil pulp resembling thick gelatin had a sp.gr. of 0·921, and contained 6% alumina combined with 30% fatty acids, together with 15% lard oil and 48% paraffin oil (Oil and Colourman's Journ. **4**, 403; *see also* J. Stich, Pharm. Zentr. 1922, **63**, 261). The oleate is also used in waterproofing fabrics.

Aluminium palmitate is a constituent of oil pulp. It may be prepared from palm oil in the same manner as the oleate. It forms a resinous, elastic, inodorous, neutral substance, insoluble in water, but readily soluble in petroleum and turpentine. K. Lieber (Dingl. poly. J. 1882, **246**, 155) recommends the use of the latter solution as a varnish. It imparts a glossy appearance to paper, leather, etc., and renders them waterproof without affecting their elasticity.

The compounds of aluminium with the higher fatty acids are used for increasing the viscosity of mineral lubricating oils, under the names "oil pulp" and "fluid gelatin" (L. Marquardt, Z. anal. Chem. 1886, **25**, 159).

Aluminium stearate, which is obtained by precipitating Al sulphate with Na stearate, or by dissolving Al hydroxide in molten stearin, is employed for thickening oils against the fall in viscosity which normally accompanies a rise in temperature, for preventing the separation of colours in made up paints, for impregnating and waterproofing cement, stonework and wood, and for giving a matt finish to oil and cellulose nitrate lacquers.

Aluminium tartrate, $Al(C_4H_5O_6)_3 3H_2O$, has been crystallised from a solution of $Al(OH)_3$ in tartaric acid (O. Goldman, Biochem. Z. 1922, **133**, 464 ; *see*, however, H. Grossmann and A. Loeb, Z. physikal. Chem. 1910, **72**, 102). A *basic tartrate* and the *mesotartrate* have been described (I.G. Farbenind. A.-G., E.P. 348790, 1930 ; F. Heckele, Österr. Chem.-Ztg. 1928, **31**, 31).

ALUMS.

This generic name is given to an important group of double salts of the general type $R_2SO_4,R'''_2O_3(SO_3)_3,24H_2O$, where R is a monovalent metal or basic radical such as potassium, sodium, ammonium, etc., and R'''_2O_3 is a sesquioxide such as that of aluminium, iron, chromium, or manganese. R may be Tl, Cs, Rb, K, Na, and perhaps Li or Ag, as well as the radicals NH_4, NH_2OH, and alkyl ammoniums. The tervalent R''' may be Ti, V, Cr, Mn, Fe, Co, Ga, In, Ir, or Rh. S may be replaced in certain cases by Se. The alums are all soluble in water, and crystallise with twenty-four molecules of water, in forms belonging to the regular system, usually octahedra or cubes.

---

[1] For further references to these compounds see Friend, Vol. XI.

The alums which contain the sesquioxide of alumina will alone be considered here, and of these the most important are the potassium, sodium and ammonium compounds. The chemistry of the whole family is dealt with by Mellor, V, 340–357.

Potassium alum, potash alum,

$$K_2SO_4,Al_2(SO_4)_3,24H_2O.$$

This salt is found in nature as *kalinite*, in the form of fibrous crystals or as an efflorescence on aluminous minerals, and occasionally also in octahedra, at Whitby, Campsie, etc. In the Solfatara, near Naples, and the islands of Volcano and Milo, it occurs in larger quantities, being formed by the action of volcanic gases upon felspathic trachyte.

The mineral *alunite, alum rock*, or *alumstone*, is of greater importance, it is a double salt of potassium sulphate and basic aluminium sulphate, having the composition

$$K_2SO_4,Al_2(SO_4)_3,2Al_2(OH)_6;$$

and is found at Tolfa near Civitavecchia; at Montioni in the Duchy of Piombino; at Mursaly, Munkact, and Tokay in Hungary; in the islands of Milo, Argentino, and Nipoglio (Grecian Archipelago); at Puy-de-Sancy and Madriat (Auvergne); at Marysville, Utah; at Calafatita, Spain; in Mexico; at Samsoun in Asia Minor; and in Australia. An "alum mountain," composed of this mineral, is reported to exist in China, and is stated to be nearly 1,900 ft. high and to have a circumference at its base of about ten miles (U.S. Cons. Report, 1903).

Until forty years ago alum was the most largely used and important compound of aluminium, and is still extensively used as a mordant in the dyeing industries, and in the production of such aluminium mordants as the acetate, sulphoacetate, etc., employed in dyeing and printing and for shower-proofing fabrics. It is also employed in the manufacture of lake pigments, in the dressing of skins ("tawing") to produce white leather, in sizing paper, and in the production of fire-proofing materials. In most of its applications, however, it is being replaced by aluminium sulphate, the use of which is considerably more economical, and most of the methods for the technical preparation of alum are now only of historical significance. It is still employed, however, in preference to the sulphate of alumina for sizing the finest papers, as a mordant for the more sensitive colours, *e.g.* alizarins, and in making glacé kid. But its continued use is more to be ascribed to the conservatism of the consumers than to any advantages that it may possess.

The manufacture of alum is of great antiquity. In the time of Pliny alum was in use as a mordant for the production of bright colours, and was even tested by means of the tannin in pomegranate juice to ascertain its purity. It was prepared in the thirteenth century at Smyrna from alum rock and since the fifteenth century has been largely produced at Tolfa near Rome from the same substance.

Very pure alum is prepared in small quantities at Solfatara. The natural alum found there is digested with water in large wooden vats under cover, and maintained at about 40° by the natural heat of the soil. The solution is decanted and crystallised. A second crystallisation produces extremely pure alum. The preparation of alum from alunite is an industry which dates from very early times. Of Oriental origin, it appears to have been introduced into Europe in the thirteenth century and during the fifteenth century several alum works were established. Amongst these may be mentioned the celebrated works at Tolfa near Civitavecchia, a district in which alum manufacture still ranks as an important industry.

The outline of the Tolfa process given below is of historical interest. The mineral, broken into lumps of moderate size, is calcined at a low red heat, either in heaps or in kilns. The operation requires to be carefully performed, and is stopped as soon as the mineral begins to evolve acid fumes. The calcination occupies about six hours and results in a loss in weight amounting to about 33%, chiefly due to the expulsion of water; at the same time the basic sulphate is decomposed, yielding alum and insoluble alumina. The roasted mass is transferred to brickwork bins and exposed to the air for several months, during which time it is occasionally moistened. The resulting sludge is lixiviated with water at 70°, and the clear decanted liquor concentrated. The crystals of alum which separate on cooling are cubic and have a reddish tinge owing to the presence of suspended ferric oxide; this may be removed by recrystallisation. The amount of soluble iron present is stated to be less than 0·005%. The product, known as Roman alum, was in former times highly valued on account of its great purity.

In the modern process, employed on the Continent, the alunite is calcined at a higher temperature and the product treated with sulphuric acid, whereby aluminium sulphate is formed from the excess of alumina, and passes into solution together with the alum. The latter is either crystallised out and the more soluble aluminium sulphate recovered as such from the mother liquors, or sufficient potassium sulphate is added to convert the whole of the aluminium sulphate into alum.

According to C. Schwartz (Ber. 1884, **17**, 2887), the best temperature for the roasting is 500°, and the acid used should have a density between 1·297 and 1·530. L. Geschwind, however, states that in France a temperature of about 1,000° is employed. Whatever the temperature, it must be such as to induce in the calcined product a permanent granular structure. A product which disintegrates to form a sludge impervious to the acid is less desirable than a nominally insoluble but easily penetrated granular mass.

Alternatively, the alunite may be extracted directly with H_2SO_4 of suitable concentration in open or closed ovens at 100°–300°.

Formerly, the greater portion of the alum manufactured in England was prepared from alum shale (alum ore), alum schist, and similar minerals, which occur in large quantities at Whitby in Yorkshire, Hurlet and Campsie in Scotland, in Sweden, Norway, Belgium, and in several parts of Thuringia, Westphalia, etc. These minerals are mixtures of aluminium silicate, iron pyrites, and bituminous substances. They were mixed with coal, made into heaps, ignited and allowed to burn, the temperature being regulated by pumping water over the surface at regular intervals. After calcination, the mass was allowed to lie until ferrous sulphide was oxidised to ferrous sulphate and ferric oxide, lixiviated with water, the aqueous extract concentrated to a specific gravity of about 1·4, treated with the correct amount of **KCl** crystals which were dissolved by stirring, the alum crystallised, washed, and recrystallised.

In the later process used by Spence the calcined shale was extracted at 110° with sulphuric acid, *d* 1·35, for 48 hours, treated with ammonia, and the ammonium alum crystallised.

In the modern processes the starting materials are almost exclusively clay, or another silicate, or bauxite (*v. Aluminium sulphate*). The silicates are roasted to remove water and organic impurities, finely milled, sieved and treated with sulphuric acid (*d* 1·53) at 70°–110° in lead-lined vessels. After cooling, the $Al_2(SO_4)_3$ is extracted with successive small portions of water, the aqueous extract concentrated, and treated hot with the correct quantity of a concentrated solution of K_2SO_4, or less frequently of **KCl** or K_2CO_3, with constant stirring. The alum deposits in fine crystals during cooling (*Alum-meal*), and when crystallisation is complete, it is separated from the mother liquor, washed with several small quantities of cold water, and recrystallised according to the purpose for which it is destined.

Many other processes have been described, *e.g.* the fusion of felspar, leucite, or nepheline with $BaSO_4$, or an alkali sulphate, at 1,500°, followed by extraction with H_2SO_4; the treatment of a finely divided mixture of bauxite and Greensand with H_2SO_4 (*d* 1·59) at 200°; or the addition of aq. K_2SO_4 to a solution of $Al_2(SO_4)_3$ prepared in the manner already described (*v. Aluminium sulphate*).

For the more delicate dyes the alum must be of extreme purity, and samples containing even less than 0·01% of iron may be unsuitable. The removal of iron offers the same difficulty here as in the case of aluminium sulphate (*q.v.*). Purity is partly ensured by crystallising in small crystals, or in the presence of sufficient H_2SO_4. Recrystallisation is effective if the iron be first reduced to the ferrous state, or removed together with other heavy metals by precipitation with, *e.g.*, aq. Na_2S or **Ca** ferrocyanide (*see* U.S. Dept. of Commerce, Bur. Min. Bull. **267**, 51).

Potash alum crystallises with 24 molecules of water, in crystals belonging to the cubic system, usually in large colourless octahedra. De Boisbaudran obtained it crystallised with hemihedral faces of the tetrahedron. The crystalline form is affected by the presence of other substances in solution and by the temperature. When formed at ordinary temperatures in the presence of basic alum, the crystals are cubes, frequently dull on the surface from the presence of the basic salt; for this reason Roman alum usually forms cubes. At 40°C., even in presence of basic salts, octahedra are produced. The crystal lattice is of the H-42 type, the cubic elementary cell of which contains 4 mols., and has an edge length $a = 12{\cdot}1$ Å. It has d^0 1·7530, d^{20} 1·7528, d^{70} 1·7444; hardness 2–2·5; m.p. 91·7°; specific heat at 15°–52°, 0·349 g.-cal.; refractive index (**Na** light) 1·4561. The values for the solubility in water obtained by different workers differ greatly. The following are those of Marino (Gazzetta, 1905 [ii], **35**, 341):

Temp. °C.	0	10	20	30	40	50	60	70	88
Solubility in g. $K_2SO_4,Al_2(SO_4)_3,24H_2O$ per 100 g. H_2O	5·70	8·49	12·03	18·49	25·00	36·78	58·54	94·38	664·0

The densities of the aqueous solutions are recorded in the table:

K alum %	4	8	12	13
$d^{17{\cdot}1}_{17{\cdot}1}$	1·0205	1·0415	1·0635	1·0690

Potash alum possesses a sweetish, astringent taste and a strongly acid reaction. The aqueous solution, especially when dilute, decomposes when heated with precipitation of a basic alum. For this reason a small quantity, not sufficient to be distinguished by taste, is frequently added to impure water. The gelatinous precipitate carries with it the colouring matter and most of the organic impurities, producing a slimy deposit.

Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. On exposure to air the crystals become white on the surface. This change is due, not to the loss of water, but to the absorption of ammonia from the air, with formation of a basic salt. Dehydrated in a vacuum at 47°, a sharp break in the rate of evolution of water occurs at the *hexahydrate* (d^{20}_4 1·676), and *anhydrous* potassium aluminium sulphate remains at 240°. Heated to dull redness in the air a porous, friable mass is obtained, only slowly soluble in water, known as *burnt alum*.

When burnt alum is mixed with one-third

its weight of carbon and heated to redness, the residue is spontaneously inflammable on account of the presence of finely divided potassium sulphide, and is known as Homberg's *pyrophorus*.

On the addition of caustic soda or sodium carbonate to a solution of alum until the precipitate at first produced is only just redissolved on agitation, *i.e.* when two-thirds of the acid has been neutralised, the solution contains a neutral basic alum, known as *neutral alum*, together with sodium sulphate. This solution, on account of the ease with which it gives up its excess of alumina to the fabric, is used by dyers as a mordant. Commercial potash alum is frequently mixed with ammonia alum.

Sodium alum, soda alum,

$$Na_2SO_4,Al_2(SO_4)_3,24H_2O,$$

occurs as *mendozite* in South America and in Japan. The technical preparation of this alum has received considerable attention because it promised to yield a cheap substitute for the more expensive potassium analogue. Unfortunately its high solubility in water, the failure of its aqueous solutions to crystallise when heated above 60°, and their tendency even in ordinary circumstances to form large, coarse crystals make its preparation and purification, especially from iron, extremely difficult; in consequence it has never had a large technical significance.

Technically, soda alum may be prepared in the following manner :—To a solution of aluminium sulphate containing 675 g. of the crystalline salt per litre, and maintained at a temperature of 50°C. to 60°C., is added a solution of sodium sulphate containing 146 g. of the anhydrous salt per litre, until the liquid attains a density of 1·35 ; crystals of soda alum separate on cooling. The crystallisation should be effected at a temperature between 10°C. and 25°C. ; at 28°C. the formation of crystals proceeds very slowly, whilst below 10°C. separation of sodium sulphate occurs (Augé ; J. 1890, 2635, D.R.P. 50323, 1899).

Messrs. F. M., D. D., and H. Spence (E.P. 5644, 1900) prepare a solution of sodium sulphate saturated at 40°C. to 50°C., which is allowed to cool during agitation until a considerable proportion of decahydrated crystals have separated. The mixture of liquid and crystals is then run into a solution of aluminium sulphate containing the solid salt in suspension. There is thus obtained a large crop of well-defined soda alum crystals. Alternatively, the solid aluminium sulphate may be added to a suitable solution of sodium sulphate or chloride, in which either salt may be suspended in the solid state.

The alum has also been made, *e.g.*, by the action of aq. nitre cake on bauxite, clay, or alunite, or by heating clay and Na bisulphate in the presence of Ba peroxide at 300°–400°.

Soda alum crystallises in regular octahedra ; d_4^{20} 1·675, m.p. 61°–63°, n_D 1·43884. Above 20° monoclinic crystals, d 1·730, have been obtained. The solubility in water in g. $Na_2SO_4,Al_2(SO_4)_3,24H_2O$ per 100 g. water is as follows (Mousseron and Gravier, Bull. Soc. chim. 1932 [iv], **51**, 1383) :

Temp. °C.	0	5	10	15	20
g. salt .	106·4	114·2	114·8	115	116·5
Temp. °C.	25	30	35	38	45
g. salt .	121·4	126·5	131·8	133·7	121·7 [1]

Ammonium alum,

$$(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O,$$

occurs as *Tschermigite* in Bohemia, and in the crater of Mount Etna. Its preparation is analogous to that of potash alum, a solution of aluminium sulphate, prepared by any of the methods already described, being treated with the equivalent quantity of ammonium sulphate and the alum separated and purified by crystallisation.

Ammonia alum crystallises in regular octahedra. The crystal lattice, like that of potash alum, belongs to the H-42 type. The elementary cell contains 4 molecules, and the edge length a is 12·16Å. It has d_4^{20} 1·645, m.p. 92°–95°, n_D 1·4591. The solubility is given below (J. Locke, Amer. Chem. J. 1901, **26**, 174).

Temp. °C.	0	10	20	30	40	50	60	70	80	90	100
Solubility in g. $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ per 100 g. H_2O	3·90	9·52	15·13	22·01	30·92	44·10	66·65	90·67	134·47	209·31	357·48

When heated the crystals swell and form a porous mass, losing water and sulphuric acid ; at a high temperature alumina alone remains. This serves as a useful method for the production of very pure alumina.

In its general properties and uses ammonia alum closely resembles the corresponding potassium compound.

Chromium alum.—See under CHROMIUM, COMPOUNDS OF.

Iron alum.—See under IRON, COMPOUNDS OF.

T. G. P.

ALUMINON, ammonium aurinetricarboxylate, forms a red lake with aluminium compounds (*v.* ALUMINIUM).

ALUMNASOL *v.* ALUMNOL.

ALUMNOL. *Alumnasol.* Trade name for aluminium β-naphtholdisulphonate,

$$Al_2[C_{10}H_5(OH)(SO_3)_2]_3.$$

Astringent and antiseptic.

ALUM ROCK, ALUNITE, ALUMSTONE *v.* ALUMINIUM.

---

[1] Turbidity develops in the solution above 40°.

ALUMS *v.* Aluminium, Compounds of.

ALUM-SHALE. A kind of shale or slate containing disseminated pyrite, which, on prolonged exposure to the weather, gives aluminium sulphate, owing to the action of sulphuric acid (from the decomposition of the pyrite) on the clayey material. The heaps of weathered shale are leached with water, and to the solution of aluminium sulphate and sulphuric acid so obtained potashes are added. The alum obtained by the evaporation of this solution is purified by recrystallisation. The alum-shales of Liassic age on the coast of Yorkshire, in the neighbourhood of Whitby, have been largely worked by this method since the time of Queen Elizabeth, but now the industry has become extinct. At Alum Bay in the Isle of Wight clays of Tertiary age were formerly used in the manufacture of alum, as early as 1579; and in the early part of the eighteenth century the Kimmeridge clay in Kimmeridge Bay, Dorsetshire, was also so used. Pyritous shales of Carboniferous age were formerly worked at Hurlet in Renfrewshire, large works for the extraction of alum having been erected there about the year 1800. Alum-shales in the coal-measures of the West Riding of Yorkshire are, however, still worked to a small extent near Rotherham, Barnsley and Darton. Here the pyrite is more efficiently and quickly oxidised by roasting the shale, which is afterwards steeped in shallow pits and the concentrated liquor treated with potassium chloride.

Reference.—"Special Reports on the Mineral Resources of Great Britain," Vol. 5, Mem. Geol. Survey, London, 1916. *V. Alums*, art. Aluminium. L. J. S.

ALUNDUM. The name "Alundum" is the trade-mark adopted about 1902 by the Norton Company of Worcester, Mass., for a highly aluminous product obtained by electrically fusing bauxite. Like some other electric furnace products, *e.g.* Carborundum, it was originally intended for use as an artificial abrasive, as a substitute for emery, and this still constitutes one of its principal applications. According to a description of the process of manufacture, crude bauxite is calcined in a rotary calciner, 60 ft. long, heated by two gas-producers, with an output of 40 tons a day. The calcined ore is fused in a special furnace consisting of a series of conical pots, mounted on cars, heated by vertical electrodes which can be raised as the fused bauxite fills the pots. In the furnace room, 2,000 electric horse-power are used and the size of the furnace is adjusted so that the fused mass does not extend to the water-cooled shell. During fusion, the iron compounds in the bauxite are reduced by the carbon electrodes and combine with 5 to 12% of silicon, and these "pigs," weighing about 3 tons, are used for the production of ferro-silicon. When the fusion is complete, the furnace is run under an electric crane which lifts the fused mass on to the cooling floor. When cold, the mass is broken up, fed into a crusher and passed over a reel to remove the fine dust which is re-fused. The lumps are then sorted and material up to standard passed on to the various processes incidental to the manufacture of grinding wheels. In addition to its use as an abrasive, alundum is employed for the production of various pieces of common laboratory apparatus, such as muffles, crucibles, extraction thimbles, etc. The value of the material for these purposes lies in its high melting-point, thermal endurance, considerable mechanical strength, high thermal conductivity compared with fireclay, and porosity. This last physical property is utilised in filtration, and alundum Gooch crucibles can be used without an asbestos filter layer and the porosity can be regulated so that the finest precipitates, such as deflocculated graphite, can be collected. Such filter layers are manufactured by mixing suitably graded alundum with a refractory binder, moulding, and firing in a ceramic kiln.

About 1909, alundum was suggested as a refractory material on account of its high melting point, relatively high thermal conductivity, and its resistance to chemical attack, *e.g.*, for the manufacture of zinc retorts and other articles where high heat conductivity is an advantage. It is stated that alundum bricks have been tested in basic open hearth furnaces and do not appear to be affected by the slags produced and that they have been tried with some success in place of silica bricks in the roofs of electric furnaces.

Alundum is made in different degrees of purity, either as a white crystalline substance, consisting of 99% of aluminium oxide, or as a reddish-brown vitreous product with 6 to 8% of impurities, mainly oxides of iron, titanium and silicon. The former material melts at 2,050°C. and has a linear coefficient of expansion of ·0000078, while the latter melts about 50°C. lower and has a slightly larger expansion of ·0000085. Alundum does not soften within 100°C. of its melting-point. Its chemical resistance to slags has been mentioned and it is stated that bonded articles when treated with sulphuric or hydrochloric acid lose 0·03% of their weight, but afterwards are quite unaffected. The following table summarises some of the more useful physical data for the material:

Melting-point (pure variety), 2,050°C.
Specific gravity, 3·93–4·01.
Hardness (Moh's scale), 9–10.
Specific heat, 0·183 to 0·200 at 100°C.
Heat conductivity 0·00833 C.G.S. units (range 650°–1,250°C.).
Electrical resistivity:

°C.	ohms./c.c.
20	9×10^6
800	30,800
1,000	7,600
1,200	2,300
1,600	190

Reference.—L. E. Saunders, Amer. Electrochem. Soc. 1911, **19**, 333; Met. and Chem. Eng. 1911, **9**, 258; J.S.C.I. 1911, **30**, 686; Norton Company, Worcester, Mass., Trade catalogue. W. C. H.

ALUNITE or ALUM-STONE. Hydrated basic sulphate of aluminium and potassium,

$KAl_3(SO_4)_2(OH)_6$, containing theoretically 11·4% of K_2O. The potassium may, however, be replaced isomorphously by sodium with a passage from "kalioalunite" to "natroalunite" (analysis VI). Further, the material is often impure owing to admixture with silica and clayey matter. The mineral is usually found as white, grey, or pinkish, compact and granular masses, somewhat resembling chalk, limestone, or marble in appearance. Sp.gr. 2·58–2·75. Occasionally, minute glistening crystals, which belong to the rhombohedral system, are found in cavities in the massive material. The following analyses are of material from I and II Bullah Delah, New South Wales (I pale pink, and II chalky white, containing more silica); III and IV, Marysvale, Utah (III of selected clear pink, translucent, coarsely granular material, and IV of compact, fine-grained, porcelain-like material); V, "calafatite" from Benahadaux, Almeria, Spain; VI, white, chalky "natroalunite" from Funeral Range, Death Valley, California.

	I.	II.	III.	IV.	V.	VI.
Al_2O_3	37·52	37·37	37·18	34·40	37·98	38·46
Fe_2O_3	0·26	0·27	trace	trace	—	—
K_2O	9·51	5·68	10·46	9·71	9·64	1·04
Na_2O	1·12	1·08	0·33	0·56	—	6·83
SO_3	36·76	22·09	38·34	36·54	34·77	25·03
SiO_2	1·92	19·34	0·22	5·28	—	10·27
P_2O_5	trace	trace	0·58	0·50	—	—
H_2O	13·19	13·86	12·90	13·08	17·61	17·60
Moisture	0·06	0·46	0·09	0·11	—	—
	100·34	100·15	100·10	100·18	100·00	99·23

The mineral mostly occurs in connection with volcanic rocks, having been formed by the action of solfataric vapours on such rocks. In some cases, however, it may have been formed by the action of decomposing iron-pyrites on clay. Extensive deposits have long been known at Tolfa near Rome, Montioni in Tuscany, and Musaz and Beregszász in Hungary. An important deposit, forming wide veins in volcanic rock (andesite or dacite), has been discovered and mined near Marysvale in Utah. A detailed description of this, together with a *résumé* of the published descriptions of other deposits of commercial importance, has been given by B. S. Butler and H. S. Gale (Bull. U.S. Geol. Survey, 1912, No. 511, pp. 1–64). Other localities are in Colorado, Nevada, California and Arizona; Kyuquot Sound, Vancouver Island, British Columbia; Bullah Delah, 60 miles north of Newcastle, New South Wales; Carrickalinga Head, on St. Vincent Gulf, 40 miles south of Adelaide, South Australia; Warnertown, near Port Pirie, South Australia; and near Sunbury, Victoria. (On the Australian deposits, *see* E. F. Pittman, "The Mineral Resources of New South Wales," Dept. of Mines, N.S.W., 1901; "The Alunite Deposits of Australia and their Utilisation," Advisory Council of Science and Industry, Commonwealth of Australia, Bull. No. 3, Melbourne, 1917.) Extensive deposits have also been found near Benahadaux, 10 km. from the port of Almeria in Spain (S. Calderón, Los minerales de España, 1910, 2, 205). A large deposit of natroalunite ("alkanasul") has been found near Salamanca in Chile (J. Westman, Bol. Minero, Santiago de Chile, 1931, **43**, 433).

Since the fifteenth century this mineral has been exploited at Tolfa near Rome, for the manufacture of potash-alum; and the harder and more compact varieties from Hungary have been used for millstones. Now, however, the mineral is of considerable importance as a source of potassium salts. When ignited, it gives off all its water and three-quarters of its sulphuric acid, there remaining alumina and potassium sulphate. By this method 92% of the latter is capable of extraction in solution. When roasted at a lower temperature, aluminium and potassium sulphates can be extracted by lixiviation and crystallised as potash-alum. Details of the methods of treating the mineral as practised in Australia and Utah are given in the bulletins quoted above. The mineral may be used directly as an artificial manure; but, since the potassium constituent is not present in a soluble form, better results are obtained by previous roasting. L. J. S.

ALUNOGEN. Hydrated aluminium sulphate, $Al_2(SO_4)_3,18H_2O$, occurring as a white, delicately fibrous efflorescence on shale and other rocks. It has been formed by the action on the aluminous rock of the products of decomposition of iron-pyrites. A trace of iron sulphate is often present, imparting a yellowish or reddish colour to the mineral. L. J. S.

ALVA or **ALFA** *v.* ESPARTO.

ALYPINE. *Amydricaine hydrochloride.* Trade name for the hydrochloride of the benzoic ester of tetramethyldiaminodimethylethyl carbinol hydrochloride,

$$C_6H_5{\cdot}COOC(C_2H_5)[CH_2N(CH_3)_2]_2HCl,$$

m.p. 169°. Local anæsthetic.

AMADOU, or GERMAN TINDER (*Amadou*, Fr.; *Zünderschwamm*, Ger.). A spongy combustible substance prepared from a species of fungus, *Fomes* (*Polyporus*) *igniarius*, the "false" tinder-fungus, which grows on the trunks of the oak but also on alder, willow, and various other trees. Amadou is prepared by removing the outer rind and carefully separating the yellow-brown spongy substance which lies within it. To convert it into tinder it is boiled in a strong solution of nitre, dried, beaten and the operation repeated. Sometimes, to render it very inflammable, it is imbued with gunpowder, whence the distinction of "black" and "brown" amadou.

AMALGAM. An alloy of mercury with some other metal or metals. There are four general methods for preparing amalgams:

1. Metallic mercury is brought into contact with the other metal, either in the mass or in a finely divided state at the ordinary or at a higher temperature. In this way amalgams of antimony, arsenic, bismuth, cadmium, magnesium, potassium, silver, sodium, tellurium, thorium, tin, zinc and lead may be obtained.

2. Mercury is brought into contact with a saturated solution of a salt of the metal, when part of the mercury goes into solution and the remainder combines with the liberated metal; or, preferably, zinc or sodium amalgam is

employed, when the zinc or sodium displaces the metal in the salt. By this method amalgams of bismuth, calcium, chromium, iridium, iron, magnesium, manganese, osmium, palladium and strontium may be prepared by using sodium amalgam, and cobalt and nickel by using zinc amalgam (Moissan, Compt. rend. 1879, **88**, 180; Chem. News, 1879, **39**, 84).

3. The metal to be amalgamated is placed in a solution of a mercury salt; copper may be amalgamated by this process. Copper amalgam has also been produced from ingredients in solid solution. When copper sulphate solution is mixed with hypophosphorous acid a precipitate of copper hydride slowly forms; if this precipitate is introduced into mercuric chloride solution it is converted into copper amalgam, and as copper amalgam has a very high germicidal action this reaction has been applied to the precipitation of copper amalgam inside teeth.

4. The metal is placed in contact with mercury and dilute acid; this is the method usually employed in amalgamating zinc. Iron, aluminium, palladium, nickel and cobalt may be made to combine with mercury by this process if they be placed in contact with a stick of zinc (Casamajor, Chem. News, 1876, **34**, 36; Arch. Pharm. 1878 [iii], **11**, 464; J.C.S. 1878, **34**, 474).

Amalgams are also formed when mercury is used as the cathode in the electrolysis of salt solutions; a number of metals can thus be obtained as amalgams, although they cannot be obtained directly in the free state by the electrolysis of aqueous solutions. The amalgams of the metals of the rare earths, lanthanum, neodymium, cerium, samarium and yttrium have been thus prepared. Dilute amalgams were prepared by the electrolysis of concentrated solutions of the anhydrous chlorides in ethyl alcohol, using a mercury cathode. These were concentrated by vacuum distillation. Further heating up to about 1,000°C. in oxide-lined crucibles in a vacuum furnace resulted in decomposition of the amalgam and isolation of the metal (Jukkola, Andrieth, and Hopkins, J. Amer. Chem. Soc. 1934, **56**, 303).

The conditions for the electrolytic deposition of titanium, uranium and vanadium from aqueous solutions on a mercury cathode have been investigated and the amalgams so formed studied (Groves and Russell, J.C.S. 1931, 2805).

Mercury and gallium are completely immiscible in one another just above the melting-points of the metals (Pushin, Stepanović, and Stajić, Z. anorg. Chem. 1932, **209**, 329).

The solubility of iron in mercury in the case of an amalgamated iron wire has been found to be about 0·00007% by weight, and to be practically constant between 20° and 211°C.; the solubility of nickel in mercury, determined by stirring mercury with nickel wire, was found to be 0·00014% by weight at 20°C. (Palmaer, Z. Elektrochem. 1932, **38**, 70). When iron pentacarbonyl, $Fe(CO)_5$, is slowly added to mercury at 300°C. a butter-soft, silver-white paste is formed and, on continued exposure to light, this becomes covered with a dark skin consisting mainly of iron. This paste normally contains a maximum of 10% iron. As shown by X-ray analysis, most of the iron is present as α-iron, *i.e.* as a suspension of α-iron in mercury. Similarly, if nickel-carbonyl, $Ni(CO)_4$, is added to mercury, a hard, brittle, matte-grey mass results, containing 8·83% nickel and which is stable in air. It has a cubic lattice, different from that of pure nickel.

The solubility of silver in mercury has been accurately determined over the range 20°-80°C. (Deright, J. Physical Chem. 1933, **37**, 405).

The solubility of gold in mercury has been investigated by many workers. The results of Anderson (J. Physical Chem. 1932, **36**, 2145) agree with those of Sunier and Weiner (J. Amer. Chem. Soc. 1931, **53**, 1714), Sunier and Mees (unpublished), and Parravano (Gazzetta, 1918, **48** [ii], 123), but do not agree well with those obtained by Britton and McBain (J. Amer. Chem. Soc. 1926, **48**, 593) and by Plaksin (J. Russ. Phys. Chem. Soc. 1929, **61**, 521).

The solubilities in mercury of the metals of atomic numbers 22–29 and of molybdenum, tungsten and uranium have been investigated; of these copper and manganese alone have solubilities in mercury greater than 1 in 10^7, their values being 0·0020% and 0·0010% respectively (Maxsted Irvin and Smith Russell, J.C.S. 1932, 891).

The electrical conductivities of liquid alkali-metal amalgams have been measured by the potentiometric method for liquid sodium, potassium and lithium amalgams with a capillary cell calibrated with mercury. It is concluded from the results obtained that the conduction is metallic (Boohariwalla, Paranjpe, and Prasad, Indian J. Physics, 1929, **4**, 147; Amer. Chem. Abstr. 1930, **24**, 9). The numerical values of the transport numbers of the metals, sodium, potassium, lithium, barium and bismuth in mercury are all of the same order of magnitude —about 10^{-5} (Kremann, Vagrin, and Scheibel, Monatsh. 1931, **57**, 323).

The electrical conductivity, viscosity, and density of dilute liquid amalgams of the alkaline earth metals have been studied (Paranjpe and Patankar, J. Univ. Bombay, 1933, **2**, 40).

In recent years great advances have been made in the study of amalgams, chiefly through the application of the methods of metallography (*v.* METALLOGRAPHY) and X-ray crystallography.

Special methods devised for the metallographic study of amalgams are described by Rosenhain and Murphy (Proc. Roy. Soc. 1926, A, **113**, 1) and Murphy (J. Inst. Metals, 1931, **46**, 509). *See also* Novach ("Amalgame," 1930, Berlin, Beuth Verlag).

No compounds exist in the amalgams of aluminium, lead and tellurium. Intermediate phases occur in the following amalgams: silver at 29% and 40% Ag; gold, Au_2Hg and $AuHg_2$; calcium, $CaHg_3$, $CaHg_5$, $CaHg_{10}$; cerium, $CeHg_4$; cæsium, $CsHg_2$, $CsHg_4$, $CsHg_6$; copper, at 25–28% or 30–35% ($CuHg$ or Cu_3Hg_4?); lithium, $LiHg_3$, $LiHg_2$, $LiHg$, Li_3Hg; magnesium, $MgHg$, Mg_2Hg_2?; sodium, $NaHg_2$, Na_3Hg; tin, $Sn_{12}Hg$?; thallium, Tl_2Hg_5. Details of these systems appear in Abstracts, J. Inst. Metals.

Microscopic and thermal analyses have given no evidence of the formation of cadmium-mercury compounds; X-ray examination has revealed the existence of a solid phase, Cd_3Hg, which has a body-centred tetragonal structure (Taylor, J. Amer. Chem. Soc. 1932, **54**, 2713).

Crystalline amalgams of zinc, lead, tin and cadmium are formed when rods of these metals are immersed in mercury for many days. Copper and silver form no such crystalline amalgams (Hosford, J. Dental Research, 1934, **14**, 33).

Measurements have been made of contact angles on platinum, zinc, silver, gallium and thallium amalgams (Gorodezkaja and Kabanov, Zhurnal Fizicheskoy Khimii (J. Gen. Chem. Russ.) 1933, **4** (5), 529).

X-ray analyses of silver, gold, and tin amalgams have been carried out (Stenbeck, Z. anorg. Chem. 1933, **214**, 16; Murphy and Preston, J. Inst. Metals, 1933, **46**, 507).

The Hall effect has been observed in tellurium amalgams (Wold and Hyatt, Physical Rev. 1930 [ii], **36**, 375).

Gold amalgams up to 75% gold have the same potential as mercury; alloys with more than 75% gold have practically the same potential as pure gold (Kremann and Baum (with Lämmermayr, Jr.), Monatsh. 1932, **61**, 315). Diagrams have been constructed showing the iso-potential lines in the ternary system gold–tin–mercury (Griengl and Baum, Monatsh. 1932, **61**, 330).

Electrical amalgam is made by melting together 1 part of zinc and 1 part of tin, and then adding 3 parts of mercury. An amalgam of cadmium is used in the construction of the cadmium standard cell; this amalgam and its electrical behaviour have been studied by A. E. Smith (Phil. Mag., February, 1910).

Silvering amalgams.—For metals, 1 part of silver to 8 parts of mercury; for glass, 1 part each of lead and tin, 2 parts bismuth and 4 parts mercury. The use of amalgams for silvering has been almost completely superseded by the use, in the case of glass, of chemically deposited silver and, in the case of metals, by electro-plating.

Dental amalgams.—A knowledge of the ternary system silver–tin–mercury is required before the problem of the setting of dental amalgams can be solved. Fundamental research on the constitution of dental amalgams and the mechanism of their setting is described by Rosenhain ("Dental Alloys," 1927, Dental Board of the United Kingdom, London). Joyner and Knight (J.C.S. 1911, **99**, 195, and 1913, **103**, 2257) and Lowry and Wilding (J.S.C.I. 1920, **39**, T, 110) are of opinion that the setting of dental amalgams is represented by the reaction:

$$Ag_3Sn+4Hg \rightarrow Ag_3Hg_4+Sn.$$

The factors controlling the setting of dental amalgams have been studied by many investigators, among them Gray, Souder and Peters, Taylor, Ward and Scott, Rothen, Paffenbarger and Sweeney, Sieglerschmidt and Arndt, Sterner-Rainer, Gayler (*cf.* Abstracts, J. Amer. Dent. Assoc.; Brit. Dent. Assoc.; Dent. Cosmos; Zahnärzt Rdsch.).

Physical tests, compression, flow, and cutting tests, together with the determination of the change in length, indicate that these properties are subject to considerable variation according to the composition of the dental alloy, and the treatment used in grinding and mixing the constituents and in preparing the amalgam; the corrosion of amalgams has been attributed to the instability of the pure phases in the solution concerned.

A specification for dental amalgam alloys has been drawn up by the U.S. Government Federal Specification Board (Federal Specification No. VA-451 (formerly No. 356), 1926) and has recently been revised ("Specifications and Certifications for Dental Materials," Paffenbarger and Sweeney, J. Amer. Dent. Assoc., April, 1934). The composition laid down for a dental alloy must be within the chemical limits: silver, 65% minimum; tin, 25% minimum; copper, not more than 6%; and zinc, not more than 2%. The specification also prescribes acceptance tests for strength and volume changes during setting. Gayler, however, suggests a still more critical composition for dental alloys—viz. that they should contain not more than 27% and not less than 25% tin (Brit. Dent. Journ. 1935, **58**, 145, and **59**, 245). Stock (Z. angew. Chem. 1928, **41**, 1182) maintains that amalgam fillings frequently cause mercurial poisoning, symptoms having been observed as the result of an absorption into the system of 0·001 milligram of mercury per day, which may readily occur with copper fillings. Fuhner (Klin. Woch. 1927, **6**, 1545) confirms the danger of copper amalgam, but states that silver amalgams are innocuous.

M. L. V. G.

AMALIC ACID *v.* ALLOXANTIN.

AMANDIN. A protein contained in the kernels of peaches and plums and in the almond, and amounts to 24% of the oil-free almond meal. Mol. wt., *v.* T. Svedberg and B. Sjögren (J. Amer. Chem. Soc. 1930, **52**, 279, A., 356). Its composition is C 51·4%, H 6·9%, N 19·0%, O 22·3%, S 0·4%. Purified specimens do not give Molisch's reaction, and it is only partially coagulated by heat. On hydrolysis it yields glutamic acid, 23·14% and arginine, 11·85% (Osborne and Clapp, Amer. J. Physiol. 1908, **20**, 470).

AMANIL DYESTUFFS (AAP) are azo dyes.

AMANITA MUSCARIA. *Fly agaric.* A poisonous fungus, used in Kamtschatka and Siberia as a narcotic and intoxicant and, when steeped in milk, as a fly poison. The narcotic organic base *muscarine* (*q.v.*) has been isolated from it.

AMARANTH. An azo-dye, the tri-sodium salt of 4-sulpho-α-naphthalene-azo-β-naphthol-3:6-disulphonic acid. The aqueous solution is magenta-red in colour. Used for dyeing and printing wool and silk, and permitted for colouring food in U.S.A. and Australia, also used as a biological stain.

AMARILLITE. Hydrated sulphate of sodium and ferric iron, $NaFe(SO_4)_2.6H_2O$, as yellow monoclinic crystals, sp.gr. 2·19, from Terra Amarilla, Copiapo, Chile (H. Ungemach, Compt. rend. 1933, **197**, 1133; Bull. Soc. Franç. Min. 1935, **58**, 200). L. J. S.

AMATIN. Trade name for 2-acetoxy-*metatoluic* acid. Antipyretic. Analgesic.

AMATOL. An explosive consisting of a mixture of ammonium nitrate (A/N) and trinitrotoluene (Trotyl ; T.N.T.), in almost any proportions, without the addition of other substances. The mixtures are distinguished by a numerical prefix, such as 80/20, 40/60, etc., the first number indicating (in this country) the percentage of A/N. In actual practice the range of mixtures does not extend beyond the two ratios already quoted, on the one hand because mixtures containing more than 80% of A/N are very difficult to detonate completely, and on the other because those containing more than 60% of T.N.T. have no advantage in cost or efficiency over the latter material alone.

Amatols in which the T.N.T. content is not less than about 50% can be prepared by melting the nitro-compound and adding the finely divided A/N which has been previously heated to the same temperature. Such mixtures tend to separate on standing and must therefore be well stirred before pouring into projectiles, mines, etc. Amatols containing a high proportion of A/N can be prepared by incorporating the two ingredients in an edge runner mill. A plastic form of 80/20 amatol and similar mixtures can be made by heating the mixture (after milling) at a temperature somewhat above the melting-point of T.N.T. in a steam-jacketed vessel provided with an agitator. Crude T.N.T. can be used for the preparation of amatols containing a large proportion of A/N, as there is little danger of oily impurities in the trotyl exuding provided that storage is not prolonged. It is essential however, in this case, that the A/N shall be free from impurities of the pyridine and thiocyanate type, as these react vigorously with the asymmetric trinitrotoluenes present in crude T.N.T., giving a copious evolution of gas. According to Robertson (J.C.S. 1921, **119**, 1), pure T.N.T. and pure A/N have practically no action on each other even at 120°C.

The amatols are powerful explosives, theoretically more efficient than T.N.T. alone, owing to the oxygen deficiency of the latter being more or less balanced by excess in the A/N. The rate of detonation, however, decreases as the percentage of A/N increases, thus reducing the shattering effect. The following table illustrates this :

	Calories per g. (water, gas).	Total gas ml. per g.	Rate of detonation m. per sec.
T.N.T. .	924	798	6,950 (at *d* : 1·57).
40/60 Amatol	920	892	6,470 (at *d* : 1·55).
80/20 Amatol	1,004	907	5,080 (at *d* : 1·50).

The theoretical proportions for complete combustion are 78·7% A/N and 21·3% of T.N.T.

The amatols are relatively insensitive to impact but can be completely detonated by the usual initiatory system of fuze and exploder ; they are thus almost ideal fillings for military projectiles. The hygroscopicity and corrosive character of the A/N ingredient, however, call for special precautions, and generally limit the use of these fillings to war-time conditions when long storage is not involved. Furthermore, the tendency of A/N to react with copper, forming explosive salts which are highly sensitive to impact and friction, precludes the use of copper or its alloys in any part of a projectile with which an amatol filling may be in contact. In the case of the "hot-mixed" amatols, the risk of contamination is somewhat reduced by the fact that each particle of A/N is coated with a film of T.N.T. H. S.

AMATOXOL. An explosive containing ammonium nitrate and *toxol*, which is a mixture of trinitrotoluene and trinitroxylene. H. S.

AMAZONITE or **AMAZON-STONE.** A bright-green variety of the potash-felspar microcline ($KAlSi_3O_8$). It is found in granitic rocks near Lake Ilmen in the Ural Mountains, at Pike's Peak in Colorado, and of very good quality in Madagascar. It is used to a limited extent as a gem-stone, and for making various small ornamental objects (*v.* FELSPAR).

L. J. S.

AMBALINE, $C_{38}H_{42}O_{10}N_2$, m.p. 123°, is a very poisonous, crystalline alkaloid from the roots of *Pycnarrhena manillensis* Vidal. It forms crystalline salts and may be written

$$C_{31}H_{25}O_4(O_2CH_2)(CO)(OCH_3)_3(NCH_3)_2$$

(Quibilan and Santos, Univ. Philippines nat. appl. Sci. Bull. 1933, **3**, 353). G. B.

AMBATOARINITE *v.* ANCYLITE.

AMBER or **SUCCINITE.** (*Bernstein*, Ger.) A fossil resin derived from the extinct conifer *Pinites succinifer* (Göppert), and found as irregular nodules in strata of Tertiary age, principally on the Prussian coast of the Baltic. The amber-bearing stratum lies partly below sea-level, and the amber washed out by the action of the waves is picked up on the sea-shore or won by dredging. Such "strand-amber" was formerly collected farther west, as far as the coast of Holland, and isolated specimens are picked up on the east coast of England (Norfolk, Suffolk and Essex). At the present time the bulk of Prussian or Baltic amber is obtained from pits and mines in the "blue earth" in Samland, East Prussia. Here the production in 1907 amounted to 404,300 kg. and in addition about 20,000 kg. was collected on the sea-shore. The annual production remains steady ; in 1930 it was 449,000 kg.

Baltic amber differs from other fossil resins in containing succinic acid, which is present to the extent of 3 to 4% in perfectly transparent specimens, but reaching 8% in cloudy ("frothy") amber. It is therefore distinguished by the mineralogical name *succinite* and in the trade the tendency is to apply the name "amber" exclusively to Baltic amber. The composition is somewhat variable, averaging **C**, 79% ; **O**, 10·5% ; **H**, 10·5% ; and corresponding approximately with the formula

$C_{10}H_{16}O$. Sulphur is also present (0·26 to 0·42%), and some ash, usually about 0·2%, but increasing in amount if the material encloses foreign matter. Amber is, however, not a simple resin ; when heated, it gives oil of amber (*q.v.*) and other products, and by the action of solvents at least four different kinds of resin can be extracted from it. According to O. Helm, Baltic amber contains 17 to 22% of a resin (m.p. 105°) soluble in alcohol ; 5 to 6% of a resin (m.p. 145°) insoluble in alcohol but soluble in ether ; 7 to 9% of a resin (m.p. 175°) insoluble in alcohol and ether but dissolving in potassium hydroxide ; and 44 to 66% of insoluble bitumen.

Baltic amber is usually pale yellow, ranging to brown or reddish-brown in colour, and it varies from perfect transparency to opacity. The varying degrees of turbidity are due to the presence of vast numbers of microscopic air-bubbles. The enclosure of insects and fragments of wood and dirt in amber is well known, and points at once to the mode of origin of the material. According to differences in colour and transparency, various trade names are applied, such as "clear," "flohmig," "cloudy," "bastard," "osseous" or "bone," and "frothy." The sp.gr. ranges from 1·05 to 1·10 (varying with the porosity) ; and the hardness is 2½, being rather higher than that of most other resins which can be scratched with the finger-nail. Refractive index n_D 1·539–1·545. The material is brittle and breaks with a conchoidal fracture. When cut with a knife, parings are not obtained, but only powder. It can be turned on the lathe and takes a good polish, being worked with whiting and water or rotten-stone and oil, and finished by friction with a flannel. When heated, amber begins to soften at about 150°, giving a characteristic odour ; it melts at 350°–375°, that is, at a higher temperature than other resins, giving dense white fumes with a peculiar aromatic odour and causing violent coughing. When rubbed it becomes negatively electrified (from the Greek name *electron*, for amber, the word "electricity" is derived) ; and when rubbed vigorously it emits an aromatic odour, but does not become sticky like other resins. These characters serve to distinguish true amber from the more abundant copal ; the latter is further usually clearer, lighter in colour, and more gummy in appearance.

In the trade the material is sorted into many grades suited for various purposes. The larger pieces of better quality ("work-stone") are cut into beads and other small personal ornaments, and are largely used for making the mouth-pieces of tobacco-pipes and cigar- and cigarette-holders. Smaller and impure fragments ("varnish") are melted down for the manufacture of amber varnish and lac ; but in recent years such material is largely converted by the application of heat and hydraulic pressure into blocks of *pressed amber* or "ambroid." About 30,000 kg. of pressed amber is now produced annually from three times the amount of rough amber ; it is cut for ornaments and mouth-pieces of pipes, etc. Prices (current in 1908) for rough "work-stone" vary, according to size and quality, from £11 to 10*s.* per kg., and for smaller, inferior material ("varnish") about 5*s.* per kg. Pressed amber fetches £4 to £5 per kg. The production and the trade in amber, as well as the literature of the subject, is almost exclusively German, though the finished articles are largely made in Vienna.

Imitations of amber are frequent. Beads of yellow glass are easily recognised ; but artificial resins (bakelite, etc.), casein products (galalith), and celluloid provide better imitations. All these have a slightly higher specific gravity than amber, and they do not fluoresce in ultra-violet rays.

Other varieties of fossil resin closely allied to amber, but regarded as distinct from Prussian or Baltic amber (succinite), are the following :

Beckerite (E. Pieszczek, 1880), a black resin occurring with Prussian amber.

Burmite, Birmite, or Burmese amber (F. Noetling, 1893), a dark reddish-brown, amber-like resin, which has long been mined in the Hukawng valley in the Myitkyina district, Upper Burma, and largely exported to China. It is found in large masses, one seen by the writer weighing 33½ lb., whilst the largest piece of Prussian amber yet found weighs only 9·7 kg. (21⅓ lb.). (H. L. Chhibber, "The Mineral Resources of Burma," 1934.)

Chemawinite (B. J. Harrington, 1891), Cedarite (R. Klebs, 1897), or Canadian amber, found as pale yellow fragments the size of a pea to that of a walnut on the beach of Cedar Lake, near Chemahawin in Saskatchewan (T. L. Walker, Univ. Toronto Studies, Geol. Ser. 1934, No. 36, 5.)

Delatynite (J. Niedźwiedzki, 1908), from Delatyn in the Galician Carpathians, differs from succinite in containing rather more carbon (79·93%), less succinic acid (0·74–1·67%), and no sulphur.

Gedrite (O. Helm, 1878), a bright, pale yellow resin found with Prussian amber, but differing from this in containing less oxygen and no succinic acid ; m.p. 140°.

Glessite (O. Helm, 1881), also found with Prussian amber ; it contains no succinic acid, but probably some formic acid ; m.p. 200°.

Romanite, Roumanite, Rumänit (Ger.), or Romanian amber (O. Helm, 1891), a brownish-yellow to brown resin, found in Tertiary sandstone at several places in Romania ; it resembles Prussian amber in containing some succinic acid (0·3–3·2%), and is characterised by the relatively large amount of sulphur (1·15%) ; m.p. 300°. Almashite and muntenite are varieties of Romanian amber described by G. Murgoci.

Simetite, or Sicilian amber (O. Helm and H. Conwentz, 1886), a clear wine-red to garnet-red resin, remarkable for its beautiful green or blue fluorescence, found in the river Simeto and other parts of Sicily. It contains only 0·4% of succinic acid.

Stantienite (E. Pieszczek, 1880), a brown resin occurring with Prussian amber.

For several papers on amber and amber-like resins, by O. Helm and by P. Dahms, *see* Schr. natf. Ges. Danzig, vols. 4–12 (1878–1908). *See also* Max Bauer, "Edelsteinkunde," 3rd ed.

1928–32, and English transl. ("Precious Stones"), by L. J. Spencer, 1904. L. Schmid, "Bernstein," 1931 (separate from C. Doelter, Handb. d. Mineralchemie, vol. 4). G. C. Williamson, "The Book of Amber," London, 1932.

L. J. S.

Amber, constitution of. Attempts have been made to determine the constitution of this resin, the principal being that of Tschirch and his pupils (Helv. Chim. Acta, 1923, 6, 214). They claimed to have isolated an acid, $C_{20}H_{30}O_4$, melting at 122° from succinite, and one, $C_{19}H_{28}O_4$, melting at 120° from gedanite. To each, unfortunately, the name *succinoxy-abietic acid* was assigned. Other bodies of very high molecular weight were separated, but as the results of ultimate analysis are the principal evidence of formulæ adduced, too much reliance cannot be placed upon their chemical individualities. What is clear is that some succinic acid in the form of esters is present. Genuine amber has an acid value 15 to 35 and an ester value 70 to 95. Dichlorhydrin is a fairly good solvent for amber, which is insoluble in most solvents until it has been melted. E. J. P.

"AMBER." Trade name for Canadian mica.

AMBER, ESSENTIAL OIL OF (*v.* Oils, Essential). When amber is heated it softens, fuses, and gives off succinic acid, water, oil, and a combustible gas. If the residue be more strongly heated, a yellowish oil passes over. Genuine oil of amber so obtained has sp.gr. of 0·915–0·950, and an optical rotation of +22° 30′ to +26°. This oil is no longer obtainable in commerce.

Commercial oil of amber is obtained by the destructive distillation of colophony resin at high temperatures. This product shows somewhat wide variations in character, but usually has sp.gr. 0·850 to 0·875, opt. rot. −12° to +12°, and refractive index 1·462 to 1·483. It is soluble in 5 to 10 volumes of 90% alcohol (Cocking, Perf. and Essent. Oil Rec. 1930, 21, 477). C. T. B.

AMBERGRIS. Ambergris was, from the ninth century onwards, valued considerably as a perfume material. It also served—and in the East still serves—the purpose of an aphrodisiac. Its origin was entirely a matter of speculation, as it was only collected on the sea-shore. It is usually considered that it is a morbid secretion in the intestines of the sperm whale (*Physeter macrocephalus*), and probably only of the male whale. It appears only to be formed when the whale is feeding on cuttle-fish (*Elodone moschata*), and according to Gattefossé ("Parfumerie Moderne," 1920, 259) the constituents of ambergris exist ready formed in the cephalopod. Large numbers of small fragments are collected on the shores of various countries, chiefly in Australia and New Zealand and on the shores of the Indian Ocean. It is probable that the presence of the small calculi is normal and that they are passed in the fæces of the whale. When some as yet unknown disease, probably of a micro-organic origin, attacks the whale, the calculi become large and, unless they are accidentally got rid of, cause the death of the whale. The best ambergris is known as grey ambergris, which will sometimes fetch as much as 120*s.* per oz. Black soft ambergris is of the poorest quality and is valued at from 5*s.* to 10*s.* per oz. Numbers of the beaks or mandibles of the cuttle-fish are almost invariably found in lumps of genuine ambergris. Reported finds of very large pieces of ambergris are usually incorrect and the substance proves not to be ambergris at all. But a piece weighing 184 lb., measuring over six feet in girth, was found in New Zealand a few years ago. It had obviously come from the stomach of a dead whale, as it could never have got into the lower intestines. In the ordinary way large pieces of ambergris are only obtained from regular whaling stations where the sperm whale is caught and cut up. Ambergris contains about 25% of a subtance known as ambrein (*q.v.*), the larger portion consisting of a fat-like body which has the formula $C_{26}H_{43}OH$, and which resembles cholesterin (Schimmel, Bericht, Oct. 1916).

Ambergris has m.p. 60°–65°, softening at 45°–55°; m.p. of ether extract, 82°–86°; $d^{15\cdot5}$ 0·900 to 0·935; saponification value of ether extract, 17 to 35; iodine value of ether extract, about 78. A synthetic perfume, the methyl ether of nitro-dibrom-butyl-*m*-cresol, m.p. 100°, has a pronounced ambergris odour.

(*See* F. R. Morrison, Bull. No. 15, Technological Museum, Sydney, 1929; A. C. Stirling, Chemist and Druggist, March 17, 1934; H. I. Cole, Perf. and Essent. Oil Rec. 1922, 300; J. Gattefossé, "Parfumerie Moderne," 1920, 259; and E. J. Parry, "Cyclopedia of Perfumery," Vol. I, 38.) E. J. P.

AMBERITE. A 42-grain smokeless shot-gun powder originally manufactured by Curtis and Harvey. Amberite No. 2 contained nitrated cotton (partly soluble and partly insoluble), 71·0%; potassium nitrate, 1·2%; barium nitrate, 18·6%; wood meal, 1·4%; paraffin jelly, 5·8%; and volatile matter, 2%. Amberite No. 1 contained nitroglycerin as well as nitro-cotton and other substances. H. S.

AMBLYGONITE. Fluo-phosphate of aluminium and lithium, $AlPO_4,LiF$, crystallising in the anorthic system. It is usually found as whitish cleavage masses much resembling felspar in appearance, from which it is distinguished by its higher sp.gr. (3·01–3·09) and chemical characters. It occurs in granitic rocks at Montebras in France, Cácares in Spain (with tin ore), Pala in California, Black Hills in South Dakota, Maine, south-east Manitoba, etc. At each of the places named it has been mined for the preparation of lithium salts, the phosphate being a by-product. It contains about 10% of lithia. A variety in which the lithium is largely replaced by sodium has been found as greyish-white cleavage masses in pegmatite near Canyon City in Fremont Co., Colorado, and named *natramblygonite* or *fremontite*. In another variety, known as *montebrasite* from Montebras in France, hydroxyl largely replaces the fluorine. The general formula for the mineral is then

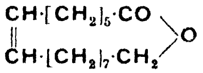
$$\mathrm{(Li,Na)Al(F,OH)PO_4}.$$

L. J. S.

AMBREIN. This body was isolated from ambergris (*q.v.*) in 1820 by Pelletier and Caventou, and was stated to have the following percentage composition: carbon, 81·74%; hydrogen, 13·32%; and oxygen, 4·94%. Riban (Compt. rend. 1912, **154**, 1729) investigated it more closely and, after recrystallisation from alcohol, found it to melt at 82°–86°. Ultimate analysis pointed to the formula $C_{23}H_{40}O$. The substance remains superfused for a considerable time, even when sown with crystals. Riban described it as optically inactive, and prepared a bromine derivative to which he assigned the formula $C_{23}H_{32}Br_8O$, and an ill-defined chlorine derivative, $C_{23}H_{35}Cl_5O$. According to Suzuki (Japan J. Med. Sci. 1925 [ii], 1), ambrein is present in ambergris to the extent of about 25%, and melts at 83°, is optically active in alcoholic solution, and may be a sterol or a sterol derivative. From the results of ultimate analysis he assigns to it the formula $C_{26}H_{44}O$, but molecular weight determinations do not harmonise with the analytical results.

E. J. P.

AMBRETTE. *Musk mallow.* The seeds of the Indian plant *Abelmoschus moschatus* (also known as *Hibiscus abelmoschus* L.), no longer of medicinal interest, are used in perfumery. The essential oil, musk kernel oil, contains farnesol, but its characteristic musk-like odour is due to *ambrettolide*,



$$\begin{array}{l}CH\cdot[CH_2]_5\cdot CO \\ \| \\ CH\cdot[CH_2]_7\cdot CH_2\end{array}\Big>O$$

b.p. 185°–190°/16 mm., the lactone of *ambrettolic acid* (*o*-hydroxy-$\Delta\zeta$-hexadecenoic acid), m.p. 25° (Kerschbaum, Ber. 1927, **60** [B], 902). This is extracted from the oil or manufactured synthetically (G.P. 449217), and sold as a concentrated perfume.

AMBRETTE-MUSK. Artificial musks of the type of a dinitro-*iso*butyl-*m*-cresyl methyl ether, m.p. 84°–86°,

$$C_6H(CH_3)(OCH_3)(NO_2)_2\cdot CH_2\cdot CH(CH_3)_2$$

(Schnaufer and Hupfeld, B.P. 18521 (1888); Baur, Compt. rend. 1890, **111**, 238) *see also* E. J. Parry, "The Chemistry of Essential Oils," vol. II, 3rd ed., 1919, London.

AMBRETTOLIDE *v.* AMBRETTE.

AMBRINE. A name given to a preparation of hard paraffin wax containing 5% of oil of amber, used in the Great War in the treatment of burns; m.p. 38°–53°.

AMBRITE. A brown translucent resin, similar to retinite, found in association with New Zealand coal (*v.* RESINS).

AMBROID *v.* AMBER OR SUCCINITE.

AMBROSIA ARTEMISIFOLIA (Fam. Compositæ). Ragweed. The weed contains a bitter glucoside and a green-coloured essential oil, sp.gr. ·876. The pollen is a frequent cause of hay fever. Ambrosia is the name of a succulent fungus cultivated by a wood-boring beetle also named Ambrosia (Fam. Scolytidæ).

AMEISINE. Trade name for Aluminium formate.

AMENYL. Trade name for the *hydrochloride* of *methyl hydrastimide*. Forms yellowish needles, m.p. 227°. Soluble in hot water or alcohol.

"AMERICAN ALLOY" *v.* ALLOYS, LIGHT.

AMERICAN ASHES. Crude potassium carbonate.

AMERICAN PARIS WHITE. Chalk (calcium carbonate) used in paints and for making putty.

AMERICAN VERMILION. Basic lead chromate, a scarlet pigment used in paints.

AMEROID (trade name). A casein plastic material made in the form of sheets, rods, and tubes (*v.* PLASTICS, CASEIN).

E. E. W.

AMETHYST. A purple transparent variety of crystallised quartz (SiO_2), used as a gemstone. So named, from ἀμέθυστος, "not drunken," owing to the ancient belief that the stone when worn as a charm prevented intoxication (*v.* QUARTZ).

L. J. S.

AMETHYST. Trade names for tetramethylsafranine and tetraethylsafranine (*v.* AZINES).

AMETHYST, ORIENTAL *v.* CORUNDUM.

AMIANTHUS. A name for the finer kinds of asbestos (*q.v.*).

AMIDE POWDER. This was one of the earlier types of smokeless powder. It contained ammonium nitrate, 35–38 parts; potassium nitrate, 40–46 parts; and charcoal, 14–22 parts. On ignition potassamide, which is volatile at high temperatures, is probably formed and the explosive on burning leaves only a small residue. It was used by the German artillery many years ago (Gaens, B.P. 14412, 1885).

H. S.

AMIDINE DYESTUFFS (JC) are azo dyes.

AMIDINES are strong non-acid bases containing an amino- and an imino-group attached to the same carbon atom. If these groups contain alkyl substituents the free base is stable; unsubstituted amidines are stable only in the form of their salts. Amidines are obtained by the action of ammonia or an amine on the imino ether formed when dry hydrogen chloride is led into an alcoholic solution of a nitrile (B.P. 343577; Hill and Rabinowitz, J. Amer. Chem. Soc. 1926, **48**, 732), *e.g.*:

$$\underset{\text{acetonitrile}}{CH_3\cdot CN} + EtOH + HCl$$

$$\rightarrow \underset{\text{acetimino-ether hydrochloride}}{CH_3\cdot C(OEt):NH,HCl}$$

$$\xrightarrow{NH_3} \underset{\text{acetamidine hydrochloride}}{CH_3\cdot C(NH_2):NH,HCl}$$

or by the action of thionyl chloride on ketoximes (Stephen and Bleloch, J.C.S. 1931, 886). Di-(*p*-ethoxyphenyl) acetamidine hydrochloride,

$$CMe(NH\cdot C_6H_4\cdot OEt):NC_6H_4\cdot OEt,HCl,$$

m.p. 189° (G.P. 80568), is the local anæsthetic *Holocaine*; amidines of this type have been prepared by Hill and Cox (J. Amer. Chem. Soc. 1926, **48**, 3214) by the action of phosphorus pentachloride on acylamino derivatives. The anæsthetic, antiseptic and hypoglycæmic properties of a number of amidines have been investigated by Easson and Pyman (J.C.S. 1931, 2991), and *N*-alkylated amidines are described by Sen and Rây (J.C.S. 1926, 646). *p*-Hydroxyphenylacetamidine (hydrochloride, m.p. 253°–254° ; nitrate, m.p. 175°–176°) has a sustained pressor action. Amidines undergo a number of condensations which are described by Mitter and Bardhan (J.C.S. 1923, **123**, 2179), Mitter and Palit (J. Indian Chem. Soc. 1925, **2**, 61), and Dox and Yoder (J. Amer. Chem. Soc. 1922, **44**, 361).

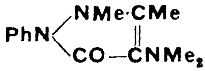
Chloroamidines are formed from amidine hydrochlorides by the action of alkali hypochlorites (Robin, Compt. rend. 1923, **177**, 1304).

Iodoamidines. Iodobenzamidine is obtained from benzamidine by the action of iodine and sodium hydroxide (Bougault and Robin, Compt. rend. 1920, **171**, 38 ; 1921, **172**, 452). It melts at 117° and appears to be a derivative of hypoiodous acid, the iodine being directly linked with nitrogen and completely liberated by potassium iodide in the presence of hydrochloric acid.

AMIDO ACID BLACK, AMIDO AZO BLACK, AMIDO BLACK, AMIDO BLUE, AMIDO BRILLIANT RED, AMIDO DISCHARGE BLACK, AMIDO DISCHARGE BLUE, AMIDO NAPHTHOL BLACK, AMIDO RED are azo dyestuffs (MLB).

AMIDOL. 2 : 4-Diaminophenol dihydrochloride, $C_6H_3(OH)(NH_2)_2{\cdot}2HCl$, used as a photographic developer.

AMIDOPYRINE. *Pyramidone.* Trade names for 4-dimethylaminoantipyrine,



AMIDOXYL BENZOATE. Ammonium *o*-iodoxybenzoate, $C_6H_4(IO_2)COONH_4$. Antiarthritic.

AMINES. Amines or ammonia bases are derivatives of ammonia in which one or more of the hydrogen atoms have been replaced by hydrocarbon radicals. This definition would include compounds in which the nitrogen atom forms part of a ring, as in pyrrole, pyridine, piperidine, etc., but such compounds are usually regarded not so much as amines but as individual heterocyclic systems possessing specific properties (*see* arts. Pyrrole ; Pyridine ; Quinoline, etc.), and come within the scope of this article only in so far as they possess the general characteristics of the ammonia bases.

Amines are classed as primary, secondary or tertiary, according as one, two or three of the hydrogen atoms of ammonia have been replaced by alkyl or aryl groups. Thus the primary amines may be represented by the general formula $R{\cdot}NH_2$, the secondary amines by the formula $RR'NH$, and the tertiary amines by the formula $RR'R''N$, where R, R', and R'' represent identical or different radicals. The chemical properties of these three classes of amine differ considerably, and their properties differ also to some extent according as the substituting radicals are (1) all aliphatic ; (2) aryl-substituted aliphatic with the nitrogen attached to the aliphatic residue as in benzylamine; such compounds behave like primary, secondary or tertiary aliphatic amines ; (3) mixed aliphatic and aromatic, with the nitrogen attached to the aromatic and aliphatic nuclei as in methylaniline ; and (4) purely aromatic amines such as aniline itself, and di- and tri-phenylamines. Substances of groups (1) and (4) will be referred to here as aliphatic or fatty amines and aromatic amines respectively. Aromatic amino-compounds serve as starting materials in the dyestuff industry, and are prepared in large quantities (*see* arts. Aniline ; Dyestuffs, Azo ; Triphenylmethane Dyestuffs ; Diphenylamine, etc.).

In addition to the primary, secondary, and tertiary amines, a fourth type of amino-compound is known, namely the fully alkylated ammonium derivatives, $[R_4N]X$, where the group $[R_4N]$ carries a positive charge like the cation $[NH_4]$ in the ammonium salts, and X is an anion such as the chlorine, HSO_4, or hydroxyl ion. Such substances are called the quaternary ammonium compounds. The salts of the amines are similarly constituted, *e.g.* $[RNH_3]Cl$, but for convenience they are frequently written in the form RNH_2,HCl.

With the exception of the vegetable alkaloids (mostly heterocyclic bases) the amines are not widely distributed in nature, though some of the lower members of the fatty series (methylamines) occur in plants and in the blood of some animals. They are, however, found as decomposition products of animal and vegetable organisms ; thus the methylamines are found in herring brine and in decomposing fish. Others, chiefly diamines, are found in the urine in certain pathological conditions and as decomposition products of animal tissues. The hydrolysis of proteins gives rise to a large number of amino-acids (*see* art. Amino-Acids), from which amines can be produced by decarboxylation. Aniline was first produced from indigo by distillation (Unverdorben, 1826), and it occurs along with a number of heterocyclic basic substances in bone-oil and coal-tar. A mixture of fatty amines, chiefly trimethylamine, is obtained by the dry distillation of the residues of the beet-sugar industry.

General Methods of Preparation.

1. *By the action of ammonia (or of primary or secondary amines) on halogen or hydroxyl derivatives of hydrocarbons, etc.*

(i) The method first described by Hofmann (Phil. Trans. 1850, **1**, 93 ; 1851, **2**, 357) of heating alkyl halides (preferably bromides or iodides) with ammonia is available for the preparation of primary, secondary, and tertiary amines of the aliphatic series, and, if aniline is substituted for ammonia, for the preparation of secondary and tertiary compounds of type (3) (above). Quaternary ammonium compounds are also formed in the reaction, which may be represented as follows :

$$RBr+NH_3 \rightarrow RNH_2,HBr$$
$$RNH_2+R'Br \rightarrow RR'NH,HBr$$
$$RR'NH+R''Br \rightarrow RR'R''N,HBr$$
$$RR'R''N+R'''Br \rightarrow [RR'R''R'''N]Br$$

The reaction takes place very slowly in aqueous solution, more quickly in alcoholic solution, but best in alcoholic solution at 100° in a sealed tube. The products obtained may contain the halogen acid salts of all the possible types of amine and the quaternary bases, and the proportions vary with the conditions of the experiment and the nature of the reactants (Werner, J.C.S. 1918, **113**, 899; 1919, **115**, 1010). In presence of excess of alkyl halide the reaction tends to yield the quaternary ammonium halide. When the reaction product is heated with excess of alkali a mixture of the free primary, secondary, and tertiary amines distils (provided that they are volatile), while the non-volatile, ionised quaternary ammonium hydroxide remains behind. The three amines in the distillate may be separated from one another (*a*) by fractional distillation (impossible in the case of the methylamines, since trimethylamine forms a constant boiling mixture with both mono- and di-methylamine); for a method of separation based on distillation under pressure with ammonia, *see* Röhm and Haas Co., B.P. 394475, 1932; separation of the three ethylamines by fractional distillation, Garner and Tyrer, J.C.S. 1916, **109**, 174; *cf. also* Price, J.S.C.I. 1918, **37**, 82; (*b*) by making use of their different modes of reaction with the chlorides of aromatic sulphonic acids, O. Hinsberg (*see later*), or, in certain cases, with oxalic ester, A. W. Hofmann (*v. infra*). It may be noted that in the Hofmann reaction a tertiary aliphatic iodide does not yield an amine, but suffers loss of hydriodic acid with formation of an ethylene hydrocarbon.

In the large-scale preparation of secondary and tertiary alkyl aryl amino-compounds, *e.g.* dimethylaniline, the primary amine is heated under pressure with an alcohol and hydrochloric acid or sulphuric acid at 180°–200°, thus obviating the necessity for the intermediate preparation of the alkyl halide. A catalytic method for preparing mono- and di-methylaniline, in which the vapours of methyl alcohol and aniline are passed over aluminium oxide at 400°–430°, is described by Mailhe and de Godon (Compt. rend. 1918, **166**, 467, 564; 1920, **171**, 1154). The toluidines and naphthylamines may be alkylated in a similar manner.

The Hofmann reaction is generally difficult to carry out when the halogen atom is directly united to an aromatic nucleus. Chlorobenzene, for example, is completely unattacked under ordinary experimental conditions by ammonia or alkylamines, this non-reactivity being a typical property of aromatic halogen compounds, and of those aliphatic halogen compounds—for example, the vinyl halides—where the halogen atom is united to an unsaturated carbon atom. The replacement of aromatic halogen atoms by the amino-group can take place, however, at temperatures of the order of 200° in presence of copper compounds, and the commercial production of aromatic amines by this method is likely to become important (*see* U.S.P. 1775360, 1930; B.P. 402063, 1932; U.S.P. 1840760, 1932). The reaction takes place readily when the nuclear chlorine atom is activated by the presence of *ortho*- or *para*-nitro groups, as for example in 2:4-dinitrochlorobenzene. *Ortho*- and *para*-nitrohalogen compounds react with urea at 240°, and the products yield the nitroanilines when boiled with alkalis (Pfister, U.S.P. 1752998, 1930).

The replacement of a halogen atom by an amino-group in the aliphatic series can also be effected by the use of sodamide or its alkyl substitution products:

$$NaNH_2+CH_3Cl \rightarrow CH_3{\cdot}NH_2+NaCl$$

(Lebeau, Compt. rend. 1905, **140**, 1042; Chablay, Compt. rend. 1905, **140**, 1262; *cf.* O. Matter, G.P. 301450, 301832). Sodamide will also react with anhydrous sulphuric esters of the aliphatic series, and with aromatic sulphonic acids to give primary amines (Jackson and Wing, Ber. 1886, **19**, 902; Titherley, J.C.S. 1901, **79**, 399; *see also* Sachs, Ber. 1906, **39**, 3006).

(ii) The replacement of a hydroxyl group by an amino-group is possible both in the aliphatic and in the aromatic series. Aliphatic amines may be obtained by heating alcohols with zinc-ammonium chloride, $ZnCl_2,NH_3$, at 250°–260° (*see* V. Merz and K. Gasiorowski, Ber. 1884, **17**, 623). W. D. Turner and A. M. Howald (J. Amer. Chem. Soc. 1920, **42**, 2663) prepare the three methylamines by heating methyl alcohol, ammonium chloride, and zinc chloride at 303°. The same reaction may also be carried out by passing a mixture of the vapour of an alcohol with ammonia or an alkylamine over thoria or tungsten oxide at 360° (P. Sabatier and A. Mailhe, Compt. rend. 1908, **148**, 898), and the reaction may be applied to compounds such as *cyclo*hexanol and benzyl alcohol (*idem.*, *ibid.* 1911, **153**, 160, 1204). This method of preparing amines is being much studied (*see*, for example, E. I. Dupont de Nemours and Co., B.P. 384714, 1931; Röhm and Haas Co., B.P. 399201, 1932; I.G. Farbenind. A.-G., B.P. 406700, 1932). Phenols are converted into primary (and secondary) amines by heating with zinc-ammonium chloride at 300°–350° (*see* Ber. 1883, **16**, 2812; 1884, **17**, 2635; 1886, **19**, 2916; 1887, **20**, 1254), or by the action of ammonia at high temperatures and pressures in presence of a catalyst, usually the chloride of a metal which can form more than one chloride (Imperial Chemical Industries, Ltd., B.P. 355715, 1930; G. T. Morgan and D. D. Pratt, B.P. 396760, 1931; F. Fischer, T. Bahr, and K. Wiedeking, Brennstoff-Chem. 1934, **15**, 101). The reaction is more facile in the naphthalene than in the benzene series, but the conversion of the naphthols into naphthylamines is usually carried out by a process due to Bucherer (J. pr. Chem. 1904 [ii], **69**, 49). The process consists in treating the naphthol with an ammonium sulphite solution containing excess of ammonia at 100°–150°, when almost quantitative conversion to the naphthylamine takes place (for mechanism of the process, *see* Raschig, Ber. 1926, **59** [B], 859). The reverse reaction, the conversion of naphthylamines into naphthols, can also be carried out by aqueous solutions of alkali bisulphites and is used technically in the case of the α-naphthylamine sulphonic acids.

Alkyl nitrates yield primary amines when treated with alcoholic ammonia at 100° (Wallach and Schulze, Ber. 1881, **14**, 421). Monomethylamine can be prepared by the methylation of ammonia in aqueous alkaline solution with methyl sulphate at 0° (Burmann, Bull. Soc. chim. 1906, **35**, 801), or by methylating phthalimide with aqueous formaldehyde and methyl alcohol at 220° and 70–90 atm. and hydrolysing the product (I.G. Farbenind. A.-G., B.P. 344971, 1929). Tertiary amines are produced by heating primary and secondary alkylamines with excess of the potassium alkyl sulphate, each in concentrated solution (M. Passon, Ber. 1891, **24**, 1678).

An interesting method of preparing ethylamine is the direct combination of ethylene and ammonia at 450° under 20 atmospheres pressure in presence of a catalyst prepared by reducing ammonium molybdate in hydrogen (I.G. Farbenind. A.-G., G.P. 479079, 1930).

Ethylene oxide combines with aqueous ammonia at 25°–30° to form chiefly tri-β-hydroxyethylamine,

$$N(CH_2{\cdot}CH_2{\cdot}OH)_3,$$

accompanied by smaller quantities of the corresponding primary and secondary bases (I.G. Farbenind. A.-G., B.P. 306563, 1927 ; Carbide and Carbon Chemicals Corporation, U.S.P. 1904013 ; *see also* Wurtz, Annalen, 1862, **121**, 227 ; Knorr, Ber. 1897, **30**, 909 ; 1899, **32**, 729). The product, after fractionation, is commercially known as *triethanolamine*, and is a viscous, hygroscopic liquid, b.p. 279°/150 mm., and finds application in the form of the neutral soaps (p_H about 8) which it forms with fatty acids. These soaps are excellent cleansing agents and emulsify a wide variety of oils, solvents and waxes (*see* Wilson, Ind. Eng. Chem. 1930, **22**, 143).

2. *By reduction of nitrogen-containing substances.*

Primary amines may be obtained by the reduction of nitro-compounds, nitroso-compounds, oximes, hydrazones, nitriles, azo- and hydrazo-compounds, amides, and amidines. Since the nitro derivatives of aromatic hydrocarbons are easily prepared by direct nitration, the reduction of nitro-compounds is the method most generally used for the preparation of primary aromatic amines. Zinin in 1842 prepared aniline from nitrobenzene by the action of alcoholic ammonium sulphide, and a modification of this method is still in use for the reduction of the dinitrobenzenes to the nitranilines. For the reduction of nitrobenzene to aniline, *v.* ANILINE. In the laboratory aromatic nitro-compounds are conveniently reduced with tin and hydrochloric acid, or with stannous chloride and hydrochloric acid ; the latter reaction may be used for the quantitative estimation of nitro-groups, or better, their reduction with titanous chloride and hydrochloric acid. Other reducing agents in use in the laboratory are iron filings and acetic acid and, in the case of alkali-soluble nitro-compounds (nitrophenols, nitrobenzoic acids, etc.) ferrous sulphate and ammonia. Sodium hyposulphite, $Na_2S_2O_4$, is also occasionally used in aqueous or dilute alcoholic solution as a reducing agent.

Nitro-compounds (also nitriles, oximes, etc.) may be reduced catalytically with hydrogen in presence of finely divided nickel or copper (Sabatier and Senderens, Compt. rend. 1902, **125**, 225), and the reduction of nitrobenzene to aniline by this means has been the subject of a large number of patents (*see* ANILINE). Nitro-compounds in alcoholic solution are easily reduced catalytically in presence of platinum or palladium at ordinary temperatures and pressures.

Nitro-compounds may be reduced to amines electrolytically in acid solution, preferably at a lead cathode. Electrolytic reduction of aromatic nitro-compounds in strong sulphuric acid leads directly to *para*-aminophenols by intramolecular rearrangement of the intermediate β-phenylhydroxylamines ; the processes described differ only in detail, and depend upon reduction in 50–90% sulphuric acid at 30°–80° with carbon or platinum electrodes, the yields being generally about 50% (Shōji, J. Chem. Ind. Tokyo, 1918, **21**, 117 ; McDaniel, Schneider and Ballard, Trans. Amer. Electrochem. Soc. 1921, **39**, 319 ; Thatcher, U.S.P. 1501472, 1924). F. M. Brigham and H. S. Lukens (Trans. Amer. Electrochem. Soc. 1932, **61**, 31) claim a 65% yield.

The reduction of nitroso-compounds, oximes and hydrazones is brought about by means of sodium amalgam in acetic acid, but the reaction is of little importance. The reduction of azo-compounds, which takes place according to the equation

$$R{\cdot}N{:}N{\cdot}R'+4H \rightarrow RNH_2+NH_2R',$$

is mainly used in the production of aromatic diamines, but can be used for the production of amino-phenols and their derivatives. Thus (G.P. 48543) by diazotising one molecule of *p*-aminophenetole and coupling with phenol the azo-compound $EtO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$ is produced, and this on ethylation and reduction gives two molecules of *p*-aminophenetole. The usual reducing agents employed for the complete reduction of azo-compounds are stannous chloride, zinc dust and acetic acid, or sodium hyposulphite.

Amides are reduced to amines with sodium in boiling amyl alcohol, but a more satisfactory procedure is to convert the amide to the thioamide by the action of phosphorus pentasulphide and to reduce this with aluminium amalgam in alcoholic or ethereal solution (K. Kindler, Annalen, 1923, **431**, 190) :

$$R{\cdot}CONH_2 \rightarrow R{\cdot}CS{\cdot}NH_2+4H \rightarrow R{\cdot}CH_2{\cdot}NH_2+H_2S$$

Aliphatic amines of high molecular weight may be prepared by the hydrogenation of the amides or ammonium salts of the acids in liquid phase using a copper-chromite catalyst (H. Adkins and B. Wojcik, J. Amer. Chem. Soc. 1934, **56**, 247).

Nitriles are reduced to primary amines (1) by zinc and hydrochloric acid (Mendius, Annalen, 1862, **121**, 129, method now obsolete); (2) by sodium in boiling alcohol,

$$R{\cdot}CN+4H \rightarrow R{\cdot}CH_2{\cdot}NH_2$$

(Ladenburg, Ber. 1885, **18**, 2957 ; 1886, **19**, 782) ; (3) in the vapour phase with hydrogen and nickel at 180°–120° (Sabatier and Senderens, Compt. rend. 1905, **140**, 482); or (4) in a solvent under pressure with hydrogen in presence of nickel (von Braun, Blessing and Zobel, Ber. 1923, **56** [B], 1988). In these reactions secondary bases are frequently produced as by-products (*see* Rupe and Hodel, Helv. Chim. Acta, 1923, **6**, 865), but this can be avoided by reducing in acetic anhydride with hydrogen and platinum oxide when the primary base is isolated as its acetyl derivative (Carothers and Jones, J. Amer. Chem. Soc. 1925, **47**, 3051), or by reducing with hydrogen and nickel at 60°–80° in presence of ferrous sulphate, when the sulphate of the primary base is produced (I.G. Farbenind. A.-G., B.P. 304000, 1927).

Hydrogen cyanide (Barratt and Titley, J.C.S. 1919, **115**, 902), alkali cyanides, and ferrocyanides (Riedel, G.P. 264528, 1913) may be reduced catalytically to methylamine.

Primary amines can be prepared by electrolytic reduction of aldehyde ammonias in acid solution (Knudsen, Ber. 1909, **42**, 3994), or by reducing solutions of an aldehyde or ketone in 7 to 8% NH_3 in absolute alcohol (1 mol.) with nickel and hydrogen under ordinary conditions of temperature and pressure (Mignonac, Compt. rend. 1921, **172**, 223).

Secondary amines may be prepared by the reduction of *iso*nitriles, or of the *Schiff's Bases* formed by the condensation of primary amines with aldehydes :

$$RNC + 4H \rightarrow RNH{\cdot}CH_3$$

$$RN{:}CHR' + 2H \rightarrow RNH{\cdot}CH_2R'$$

The latter reaction may be carried out by reducing the compound in the fused state at 170° with hydrogen and nickel, benzylideneaniline thus giving benzylaniline (Mailhe, Compt. rend. 1921, **172**, 280). Monomethylaniline is prepared by reduction of methyleneaniline by means of zinc dust and sodium hydroxide (G.P. 75854 ; F.P. 212506 ; *see also* P. F. Frankland, F. Challenger, and N. A. Nichols, J.C.S. 1919, **115**, 198), or by means of excess of formaldehyde (G. T. Morgan, E.P. 18081, 1915). The latter reaction is a special case of the methylation of ammonia or amines by means of formaldehyde, when the reaction can be made to yield mono-, di- or tri-methylamine under the appropriate experimental conditions (Eschweiler, G.P. 80520, 1893 ; Brochet and Cambier, Compt. rend. 1895, **120**, 449, 557 ; Eschweiler, Ber. 1905, **38**, 880 ; Knudsen, Ber. 1914, **47**, 2694 ; F. Bayer and Co., G.P. 287802, 1916 ; E. A. Werner, J.C.S. 1917, **111**, 844 ; *see also* "Organic Syntheses," Vol. III, 67).

3. *From the acid amides and azides, etc.*

Primary amines may be prepared in two ways from the carboxylic acids containing one more carbon atom, *i.e.* an acid $R{\cdot}CO_2H$ is converted into an amine $R{\cdot}NH_2$, and the reactions are applicable both in the aliphatic and aromatic series.

(*a*) The Hofmann degradation of acid amides (A. W. Hofmann, Ber. 1882, **15**, 407, 762; 1884, **17**, 1407, 1920 ; 1885, **18**, 2734 ; 1886, **19**, 1822). The method consists in heating the acid amide with aqueous potassium hydroxide (about 3 mols.) and bromine (1 mol.), the final result being the formation of a primary amine, potassium carbonate, and potassium bromide. The first product of the reaction is a bromamide, which in presence of excess of potassium hydroxide undergoes a "Beckmann Rearrangement" with production of an *iso*cyanate, and this is immediately hydrolysed to the primary amine :

$$RCO{\cdot}NH_2 + KOH + Br_2 \rightarrow RCO{\cdot}NHBr + KBr + H_2O$$

$$RCO{\cdot}NHBr + KOH \rightarrow RNH_2 + CO_2 + KBr$$

The amides of the aliphatic acids containing more than five carbon atoms yield, as well as the primary amine, the nitrile of the lower fatty acid, owing to the further action of bromine on the amine,

$$RCH_2{\cdot}NH_2 + 2Br_2 \rightarrow RCN + 4HBr,$$

and the yield of amine produced decreases rapidly with increase of molecular weight. If, however, the bromamide is isolated and treated with sodium methoxide, molecular rearrangement occurs as before followed by the production of a urethane which may then be hydrolysed by heating with alkali (Jeffreys, Ber. 1897, **30**, 898):

$$RCO{\cdot}NHBr + CH_3{\cdot}ONa \rightarrow RNH{\cdot}CO_2CH_3 + NaBr$$

If insufficient bromine is employed acyl-alkylureas are produced, *e.g.* acetamide gives methylacetylurea, $CH_3{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_3$. An important application of the Hofmann degradation in the aromatic series is the production of anthranilic acid from phthalimide, which first undergoes opening of the ring to give phthalamic acid ; the reaction is also of particular value in the preparation of the bases of the type of benzylamine.

(*b*) The Curtius degradation of acid azides (Curtius, Ber. 1894, **27**, 779 ; 1896, **29**, 1166 ; Forster, J.C.S. 1909, **95**, 433). An acid azide (formed from the ester by treatment with hydrazine, and acting upon the resultant hydrazide with nitrous acid) is boiled with alcohol when nitrogen is evolved, and the product undergoes molecular rearrangement and combines with alcohol to give a urethane :

$$RCON_3 + EtOH \rightarrow RNH{\cdot}CO_2Et + N_2$$

which is subsequently hydrolysed by boiling with hydrochloric acid.

A reaction very similar to the Curtius degradation is the production of a primary amine by treating a sulphuric acid solution of a carboxylic acid with a solution of hydrazoic acid in benzene :

$$RCO_2H + N_3H \rightarrow RNH_2 + CO_2 + N_2$$

The reaction is applicable to both aliphatic and aromatic acids, and to aliphatic dibasic acids, and the yields in general are high (K. F. Schmidt, Ber. 1924, **57** [B], 704 ; Chem. Zentr. 1926, I, 2511 ; 1927, I, 1368 ; von Braun, Annalen, 1931, **490**, 125; Oesterlin, Angew. Chem. 1932, **45**, 536).

Another somewhat similar reaction is the conversion of a ketone, $RCO{\cdot}R'$, through the oxime, $RC(:NOH)R'$, to the acylamino derivative, $RNH{\cdot}CO{\cdot}R'$ (*or* $RCO{\cdot}NHR'$), by the Beckmann rearrangement, and hydrolysis to the amine RNH_2 or $R'NH_2$, *e.g.* acetophenone is thus converted into aniline and acetic acid.

4. *By hydrolysis of* isocyanates, *etc.*

Alkyl *iso*cyanates (prepared from metallic *iso*cyanates and alkyl halides) are hydrolysed by boiling with alkalis; this reaction led to the discovery of primary amines by Wurtz (Annalen, 1849, **71**, 330):

$$RN{:}C{:}O \rightarrow 2NaOH \rightarrow RNH_2+Na_2CO_3$$

and the alkyl *iso*thiocyanates, $RN{:}C{:}S$, are similarly hydrolysed with formation of the primary amines, sodium carbonate, and sodium sulphide.

*Iso*cyanides (*iso*nitriles) yield primary amines when hydrolysed with dilute hydrochloric acid:

$$RNC+HCl+H_2O \rightarrow RNH_2,HCl+HCO_2H$$

A general method for the preparation of secondary bases is described by Vliet (J. Amer. Chem. Soc. 1924, **46**, 1307; *see also* "Organic Syntheses," 1925, **5**, 43). An aqueous solution of sodium cyanamide is treated with an alkyl bromide, and the resulting dialkylcyanamide is hydrolysed with dilute sulphuric acid, the secondary base being then liberated by the addition of sodium hydroxide:

$$Na_2N{\cdot}CN+2RBr \rightarrow R_2N{\cdot}CN+2NaBr$$

$$R_2N{\cdot}CN+2H_2O \rightarrow R_2NH+NH_3+CO_2$$

5. *By hydrolysis of* N-*alkylamido compounds, etc.*

(*a*) The alkylphthalimides, obtained by treating potassium phthalimide with an alkyl halide, undergo hydrolysis with fuming hydrochloric acid to give phthalic acid and a primary amine, free from secondary and tertiary amines (Gabriel, Ber. 1887, **20**, 2224; 1891, **24**, 3104):

$$C_6H_4[CO]_2NK+RI \rightarrow C_6H_4[CO]_2NR+KI$$

$$C_6H_4[CO]_2NR+2H_2O \rightarrow C_6H_4(CO_2H)_2+NH_2R$$

Alkylene oxides will react with potassium phthalimide to give products which on hydrolysis yield amino-hydroxy compounds (Gabriel and Ohle, Ber. 1917, **50**, 804, 819). The alkylphthalimides are frequently difficult to hydrolyse with hydrochloric acid, but they yield readily to the action of hydrazine hydrate (Ing and Manske, J.C.S. 1926, 2348).

(*b*) A similar method, available for the preparation of secondary from primary amines, is due to Hinsberg (Annalen, 1891, **265**, 179). The sodium derivative of an *N*-substituted benzene-sulphonamide (derived from benzene sulphonic chloride and a primary amine) is treated with an alkyl iodide, and the product hydrolysed with hydrochloric acid at 120°–180°, or treated with hydriodic acid and phosphonium iodide (E. Fischer, Ber. 1915, **48**, 93):

$$C_6H_5{\cdot}SO_2{\cdot}NRNa \rightarrow C_6H_5{\cdot}SO_2{\cdot}NRR' \rightarrow NHRR'$$

Toluene ω-sulphonamides may also be used (Johnson and Ambler, J. Amer. Chem. Soc. 1914, **36**, 372).

Primary bases may also be converted into secondary bases by condensation with aldehydes to form the Schiff's bases, which yield additive compounds with alkyl iodides or dimethyl sulphate, and these are readily hydrolysed to give the secondary base (*see* Kindler and Peschke, Arch. Pharm. 1932, **270**, 340, 353):

$$RN{:}CHR' \rightarrow RN(MeI){:}CHR' \rightarrow RNHMe+R'CHO$$

6. *From* p-*nitroso derivatives of secondary and tertiary aromatic amines.*

Mono- and di-alkylanilines yield *p*-nitroso derivatives (the mono- with intermediate formation of the *N*-nitroso-compound) when treated with nitrous acid, and these are hydrolysed by boiling with sodium hydroxide solution to *p*-nitrosophenol and a mono- or di-alkylamine:

$$NO{\cdot}C_6H_4{\cdot}N(CH_3)_2+KOH \rightarrow NO{\cdot}C_6H_4{\cdot}OK+HN(CH_3)_2$$

Monoalkylated aliphatic diamines may be prepared by condensing a chloroalkylamine with a monoalkylaniline, converting the product into its *p*-nitroso derivative, and decomposing with alkali (I.G. Farbenind. A.-G., B.P. 292615, 1927). β-Chloroethylamine is thus converted into *N*-monomethylethylene-diamine.

7. *By decarboxylation of amino-acids.*

Aliphatic amino-acids are decarboxylated by heating with baryta:

$$CH_3{\cdot}CH(NH)_2{\cdot}CO_2H \rightarrow CH_3{\cdot}CH_2{\cdot}NH_2+CO_2$$

The same process is frequently brought about by the action of bacteria.

Anthranilic acid (and other amino-acids of the aromatic series) readily loses carbon dioxide on heating.

8. *Direct introduction of the amino-group into the aromatic nucleus.*

A number of attempts have been made to introduce an amino-group into benzene. Schmidt (E.P. 250897, 252460, 1925; U.S.P. 1564631, 1925; G.P. 427858, 1926; U.S.P. 1637661, 1927) treats benzene with hydrazoic acid in presence of concentrated sulphuric acid or other catalyst such as aluminium chloride, and obtains small yields of aniline. Curtius and Bertho (Ber. 1926, **59** [B], 565) heat a benzene solution of carbonyl azide, CON_6, at 150° and obtain pyridine and a trace of aniline, whilst Bertho (*ibid.* 589) uses ammonium azide in benzene at 260°–280° and also obtains aniline. Replacement of hydrogen by the amino-group in 1 : 3 : 5-trinitrobenzene takes place readily by the action of hydroxylamine and alkali to give picramide, and the nitronaphthalenes similarly yield amino-nitro derivatives. α-Naphthol and α-naphthylamine yield 5-aminonaphthol and 1 : 5-diaminonaphthalene respectively by heating with sodamide, and the heterocyclic bases pyrrole and pyridine similarly yield amino derivatives (*see* Houben-Weyl, "Die Methoden der Organischen Chemie," 2nd ed., 1924, **4**, 237).

General Properties.

The amines of the aliphatic series are volatile, inflammable substances, the lower members being gases or liquids with low boiling-points, very soluble in water, and strongly alkaline to litmus ; the density of the liquid members of the series is about 0·75, and increases slightly with increase in the molecular weight. Their basicity, measured by the conductivity method, indicates that they are stronger bases than ammonia, but such measurements do not give the true dissociation constants owing to the fact that solutions of bases contain the free amines as well as the corresponding hydroxides, whose dissociation constants give a true measure of their strengths as bases. T. S. Moore (J.C.S. 1907, **91**, 1373, 1379) and Moore and T. F. Winmill (J.C.S. 1912, **101**, 1635) have shown how the true dissociation constants may be obtained, and the results indicate that the alkylamines are appreciably stronger bases than ammonia (ammonia, $K=0{\cdot}341\times10^{-7}$; methylamine, $K=5{\cdot}04\times10^{-7}$; ethylamine, $K=7{\cdot}44\times10^{-7}$). They will saponify esters and precipitate oxides from the salts of many heavy metals. They have an ammoniacal and fishy odour. The smell, inflammability, boiling-point and solubility in water become less with increase in molecular weight, and the highest known members are odourless solids at ordinary temperatures. The less volatile members of the series form solid carbonates with the CO_2 in moist air. Amines of the type of benzylamine, β-phenylethylamine, *cyclo*hexylamine, etc., closely resemble the aliphatic amines of high molecular weight, but those amines in which the amino-group is in direct union with an aromatic nucleus, such as aniline, are considerably less basic than ammonia (apparent dissociation constant of aniline, $K=4\times10^{-10}$, H. T. Tizard, J.C.S. 1910, **97**, 2494) and possess certain chemical properties which distinguish them from the true aliphatic amines and the amines of the benzylamine type. The diminished basicity of the purely aromatic amines is more apparent in the case of diphenylamine, salts of which are readily hydrolysed by water, whilst triphenylamine is neutral and forms no salts with acids.

The aromatic amines are much more easily substituted by halogens, the nitro-group, and the sulphonic acid group than the hydrocarbons from which they are derived, and the substituted derivatives are of great importance in the dyestuff industry. In substituting with halogens or nitric acid it is often necessary to protect the amino-group by acetylation, and, at the same time, to diminish the reactivity of the nucleus ; the acetyl group is subsequently removed by hydrolysis.

The tables shown below give some of the physical properties of the more important aliphatic and aromatic amines, and their derivatives.

Aliphatic Amines.

Alkyl Groups.	Primary.			Secondary.		Tertiary.	
	M.p. °C.	B.p. °C.	Sp.gr.	M.p. °C.	B.p. °C.	M.p. °C.	B.p. °C.
Methyl . . .	—	−7·5	0·699 (−11°)	—	+7	—	+3·5
Ethyl . . .	−80·6	+16·6	0·708 (−2°)	−40	56	−115	89
Propyl . . .	—	50	0·719 (20°)	−63	110	—	157
iso-Propyl . .	—	32	0·690 (18°)	—	84	—	—
prim. n-Butyl .	−50·5	78	0·739 (25°)	—	160	—	216·5
iso-Butyl . .	—	66	0·724 (25°)	−77	140	−24	186
sec. n-Butyl (dl.)	—	63	0·728 (15°)	—	132	—	—
tert.-Butyl . .	−68	45	0·698 (15°)	—	—	—	—
prim.-n-Amyl .	−55	104	0·766 (19°)	—	91–93/ 14 mm.	—	130/ 14 mm.
iso-Amyl. . .	—	96	0·747 (25°)	−44	188	—	237
prim.-n-Hexyl .	−19	129	0·763 (25°)	—	192–195	—	263–265
,, Heptyl .	−23	155	0·777 (20°)	+30	271	—	330
,, Octyl .	—	191	0·777 (28°)	+36·5	298	—	366
,, Nonyl .	—	195	—	+29	—	—	—
,, Decyl .	+17	217	—	—	—	—	—
,, Undecyl.	15	232	—	—	—	—	—
,, Duodecyl	27	248	—	—	—	—	—
,, Tridecyl.	27	265	—	—	—	—	—
,, Tetradecyl	37	162/15 mm.	—	—	—	—	—
,, Pentadecyl	36	300	—	—	—	—	—
,, Hexadecyl	46	330	—	—	—	—	—
,, Heptadecyl	49	335–340	—	—	—	—	—

Aromatic Amines.

Formula.	Name.	M.p. °C.	B.p. °C.	Sp.gr.	M.p. of monoacetyl deriv. °C.
$C_6H_5{\cdot}NH_2$	Aniline	−8	+184	1·024 (16°)	+115
$CH_3{\cdot}C_6H_4{\cdot}NH_2$	*o*-Toluidine	—	199	0·999 (20°)	110
,,	*m*- ,,	—	203	0·998 (25°)	65
,,	*p*- ,,	+45	200	—	145
$(CH_3)_2C_6H_3{\cdot}NH_2$	*o*-3-Xylidine	—	223	0·991 (15°)	134
,,	*o*-4- ,,	51	226	1·076 (17°)	99
,,	*m*-2- ,,	—	216	—	177
,,	*m*-4- ,,	—	212	0·918 (25°)	129
,,	*m*-5- ,,	—	220	0·972 (15°)	138
,,	*p*-Xylidine	15	215	0·980 (15°)	139
$(CH_3)_3C_6H_2{\cdot}NH_2$	Mesidine	—	233	—	216
,,	*ψ*-Cumidine	68	235	—	164
$C_6H_5{\cdot}NH{\cdot}CH_3$	Methylaniline	—	194	0·989 (20°)	102
$C_6H_5{\cdot}N(CH_3)_2$	Dimethylaniline	1·5	193	0·958 (20°)	—
$C_6H_5{\cdot}NH{\cdot}C_2H_5$	Ethylaniline	—	206	0·964 (15°)	55
$C_6H_5{\cdot}N(C_2H_5)_2$	Diethylaniline	−21·3 and −34·4	216	0·939 (15°)	—
$C_6H_5{\cdot}CH_2{\cdot}NH_2$	Benzylamine	—	184	0·987 (15°)	61
$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	*β*-Phenylethylamine	—	197	0·958 (24°)	44
$(C_6H_5)_2NH$	Diphenylamine	+53	312	1·160 (20°)	103
$(C_6H_5)_3N$	Triphenylamine	127	348	—	—
o-$C_6H_4(NH_2)_2$	*o*-Phenylenediamine	102	257	—	186 diacetyl derivs.
m- ,,	*m*- ,,	63	287	1·139 (15°)	191
p- ,,	*p*- ,,	147	267	—	>295

In general all classes of amines form addition products with acids, containing one molecule of base to one molecule of monobasic acid. The existence of certain abnormal salts of amines recorded in the literature, *e.g.* $(CH_3)_2NH,2HCl$ (Korczyński, Ber. 1908, **41**, 4379 ; Kaufler and Kunz, Ber. 1909, **42**, 385, 2482), has not been confirmed (Hunter and Byrkit, J. Amer. Chem. Soc. 1932, **54**, 1948). Abnormal hydrofluorides of the aromatic bases are, however, known, and they are all of the type $RNH_2,4HF$ (Berliner and Hann, J. Physical Chem. 1928, **32**, 1142). The picrates and picrolonates are characteristic and are used for the identification of amines, as are also the double salts with platinum and gold chlorides, which have the general formulæ $B_2H_2PtCl_6$ and $BHAuCl_4$ respectively. Amines also form double salts with mercuric chloride and stannic chloride. Many aliphatic amines combine exothermally with water to form monohydrates, which are decomposed by potassium hydroxide or by distillation over anhydrous barium hydroxide. With alkyl halides tertiary amines form quaternary ammonium salts of the type $[NRR'R''R''']I$ when $RR'R''R'''$ may be the same or different radicals. In cases where these radicals are all different the substances are capable of existing in two enantiomorphous optically active forms (*see*, for example, W. J. Pope and S. J. Peachey, J.C.S. 1899, **75**, 1127 ; H. O. Jones, J.C.S. 1903, **83**, 1418 ; 1904, **85**, 223). Enantiomorphic modifications of the tertiary amine oxides, $RR'R''N \rightarrow O$ (*see* p. 313), have also been isolated (Meisenheimer, Ber. 1908, **41**, 3966; Annalen, 1911, **385**, 117). The rate of formation of quaternary ammonium salts from tertiary amines and alkyl halides varies with the nature of the reactants and with the solvent (Menschutkin, Z. physikal. Chem. 1890, **6**, 41 ; Wedekind, Ber. 1899, **32**, 511 ; Annalen, 1901, **318**, 90 ; Preston and Jones, J.C.S. 1912, **101**, 1930; Thomas, J.C.S. 1913, **103**, 594 ; for a full discussion of the subject, *see* " Kinetics of Reaction in Solution," E. A. Moelwyn-Hughes, Oxford, 1933, p. 106 *et seq.*). When treated with excess of moist silver oxide, the quaternary ammonium salts are converted into the very strongly basic quaternary ammonium hydroxides, $[NR_4]OH$, which readily undergo decomposition on heating, frequently even in aqueous solution. Thus tetramethylammonium hydroxide yields trimethylamine and methyl alcohol, and tetraethylammonium hydroxide yields triethylamine, ethylene, and water. This latter type of decomposition is more general than the elimination of a molecule of alcohol, and is the basis of the process known as *exhaustive methylation* (A. W. Hofmann), which has proved of great value in determining the constitution of the natural bases. Thus, if piperidine is completely methylated to the quaternary ammonium iodide, and this is converted into the corresponding hydroxide and distilled, and the process repeated, the final products are α-methylbutadiene and trimethylamine. For a discussion of the mechanism of this process, *see* Hanhart and C. K. Ingold (J.C.S. 1927, 997).

The formation of quaternary ammonium compounds by addition of excess of methyl iodide to an amine gives a quantitative method for the estimation of the number of replaceable *N*-hydrogen atoms in the substance. Analysis of the original compound and of its quaternary methyl derivative gives the number of methyl groups which have entered into the molecule.

The penta-alkylammonium compounds described by Schlenck and Holtz (Ber. 1916, **49**, 603; 1917, **50**, 274, 276), such as triphenylmethyl tetramethylammonium, formed by treating sodium triphenylmethyl with tetramethylammonium chloride, are ionised compounds of the type,

$$CPh_3{\cdot}NMe_4\,;$$

they are bright-red substances forming conducting solutions in absolute pyridine, and are decomposed by water to give a hydrocarbon (triphenylmethane) and tetramethylammonium hydroxide. The nitrogen is thus in its normal pentavalent condition, and nitrogen penta-alkyls can only be formed when one of the groups can exist in the ionised state.

The free radical tetraethylammonium, $(C_2H_5)_4N$, has been obtained as a blue solution in liquid ammonia at −70° by the electrolysis of tetraethylammonium iodide (Schlubach and Ballauf, Ber. 1921, **54** [B], 2811). It combines directly with iodine to form tetraethylammonium iodide.

Reactions.

1. *With nitrous acid.*

Primary aliphatic amines, or amines of the benzylamine type, when treated in acid solution with sodium nitrite, yield alcohols with evolution of nitrogen:

$$RNH_2+HNO_2 \rightarrow ROH+N_2+H_2O$$

The reaction, however, is not simple (reaction velocity measurements have been made by T. W. J. Taylor, J.C.S. 1928, 1099, 1897) and the alcohol is often an isomer of the expected product. Thus *n*-propylamine gives 42% of *n*-propyl alcohol and 58% *iso*propyl alcohol, and *iso*butylamine gives 75% of trimethyl carbinol (Henry, Compt. rend. 1907, **145**, 899, 1247; D. W. Adamson and J. Kenner, J.C.S. 1934, 838), and compounds such as *cyclo*butylmethylamine, *cyclo*hexylmethylamine, and *cyclo*octylmethylamine undergo ring enlargement to give derivatives of *cyclo*pentane, *cyclo*heptane, and *cyclo*nonane respectively (L. Ruzicka and W. Brugger, Helv. Chim. Acta, 1926, **9**, 399).

Secondary amines of all types when treated with sodium nitrite and a mineral acid yield non-basic nitrosamines as:

$$RR'NH+HNO_2 \rightarrow RR'N{\cdot}NO+H_2O$$

The nitrosamines regenerate the parent secondary bases when boiled with hydrochloric acid, and are reduced with zinc dust and acetic acid to dialkylhydrazines, $RR'N{\cdot}NH_2$.

Tertiary aliphatic amines react with nitrous acid to form the nitrites only, and in the case of the primary and secondary amines nitrites are undoubtedly formed as the initial products (Wallach, Chem. Zentr. 1907, II, 54; Neogi, J.C.S. 1912, **101**, 1610; 1914, **105**, 1270).

Primary aromatic amines react in cold acid solution with nitrous acid to give solutions of the diazonium salts, according to the equation:

$$RNH_2{,}HCl+HNO_2 \rightarrow [RN_2]Cl+2H_2O$$

The reaction is of great importance, since the diazonium salts are very reactive. When, for example, benzene diazonium chloride is heated with water, alcohol, cuprous chloride, cuprous bromide, cuprous cyanide, potassium iodide, stannous chloride or sodium sulphite and sulphur dioxide, there is produced phenol, benzene, chlorobenzene, bromobenzene, benzonitrile, iodobenzene, and phenylhydrazine respectively. Further, the diazonium salts *couple* with phenols, naphthols, etc., in alkaline solution to give hydroxy-azo compounds, *e.g.* $PhN{:}N{\cdot}C_6H_4{\cdot}OH$, and with aromatic amines in acid solution to give amino-azo compounds (with intermediate formation of diazoamino compounds), *e.g.* $PhN{:}N{\cdot}C_6H_4{\cdot}NH_2$. These azo derivatives are highly coloured and many are employed as dyestuffs (*see* art. Dyestuffs, Azo). The red, alkali-insoluble azo-β-naphthol derivatives formed by coupling diazonium salts with alkaline β-naphthol solutions form a simple and striking test for a primary aromatic amine.

Mixed tertiary aromatic amines react with nitrous acid to form nitroso derivatives, *e.g.* dimethylaniline yields *p*-nitrosodimethylaniline,

$$ON{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

The salt is yellow and the free base green, and is hydrolysed by boiling with aqueous sodium hydroxide to the salt of *p*-nitrosophenol, $ON{\cdot}C_6H_4{\cdot}OH$, and dimethylamine. *p*-Nitroso derivatives are also produced from the nitrosamines of secondary bases such as monomethylaniline by the action of alcoholic hydrogen chloride (O. Fischer-Hepp transformation).

2. *With chlorides of aromatic sulphonic acids.*

Primary and secondary amines when shaken in strongly alkaline solution with chlorides of aromatic sulphonic acids yield the corresponding amide; tertiary amines do not react. Of these amides, *e.g.* $PhSO_2{\cdot}NHR$ and $PhSO_2{\cdot}NRR'$ respectively, the first type only are soluble in dilute alkalis with formation of salts. The primary and secondary amines can be regenerated from the amides by boiling with concentrated hydrochloric acid or by heating with sulphuric acid at 120°–150° (O. Hinsberg, Ber. 1890, **23**, 2963; Annalen, 1891, **265**, 178). These reactions provide a generally applicable method for the separation of mixtures of primary, secondary, and tertiary bases. The *m*-nitrobenzene sulphonamides and the toluene-ω-sulphonamides of primary and secondary mixed and aliphatic amines are useful compounds for identification of the bases (Marvel, Kingsbury, and Smith, J. Amer. Chem. Soc. 1925, **47**, 166; Marvel and Gillespie, *ibid.* 1926, **48**, 2943).

3. *With carboxylic acid chlorides or anhydrides.*

Primary and secondary amines of all types react with, for example, acetyl chloride or acetic anhydride to give acetyl derivatives,

$RNH{\cdot}CO{\cdot}CH_3$ and $RR'N{\cdot}CO{\cdot}CH_3$. These compounds, as a rule, are sparingly soluble or insoluble in cold water, are generally well-defined crystalline substances of considerably higher melting-point than the bases themselves, and are frequently used for the identification of amines; the benzoyl derivatives are also used for this purpose. The parent amines may be regenerated by hydrolysis of the acyl derivatives. Aromatic amines are conveniently converted into acetyl derivatives by shaking with acetic anhydride and water. Vigorous treatment with the acylating agent may give rise, in the case of primary bases, to diacyl derivatives, *e.g.* $RN(COR')_2$. Tertiary amines combine additively with acid chlorides giving unstable products of the type $[R_3N{\cdot}COR']Cl$.

4. *With Grignard reagents.*

Primary and secondary amines react with the Grignard reagent at ordinary temperatures with evolution of the corresponding hydrocarbon, *e.g.* with magnesium methyl iodide :

$$RNH_2+CH_3MgI \rightarrow RNH{\cdot}MgI+CH_4$$
$$RR'NH+CH_3MgI \rightarrow RR'N{\cdot}MgI+CH_4$$

This reaction is the basis of Zerewitinoff's method (Ber. 1907, **40**, 2023 ; 1908, **41**, 2233) for estimating amino- and imino-groups, the volume of methane being measured. The second hydrogen atom of a primary base will react in a similar manner at higher temperatures. Tertiary amines react only partially by direct addition, giving, *e.g.*, $[R_3N{\cdot}CH_3]MgI$.

5. *With aromatic aldehydes.*

Primary and secondary but not tertiary amines readily condense with benzaldehyde or other aromatic aldehyde :

$$PhCHO+NH_2R \rightarrow PhCH{:}NR+H_2O$$
$$PhCHO+2NHRR' \rightarrow PhCH(NRR')_2+H_2O$$

The products from primary amines are known as *Schiff's Bases*, and a number of their properties have already been described ; they are readily hydrolysed by dilute acids.

6. *With chloroform and potassium hydroxide.*

Aliphatic and aromatic primary amines when warmed with chloroform and potassium hydroxide yield *iso*cyanides (carbylamines) :

$$RNH_2+CHCl_3+3KOH \rightarrow RNC+3KCl+3H_2O$$

Secondary and tertiary amines give no characteristic reaction with these reagents.

7. *With carbon disulphide.*

Aliphatic primary and secondary amines react with carbon disulphide in alcoholic solution with formation of salts of alkyldithiocarbamic acids :

$$2RNH_2+CS_2 \rightarrow RNH{\cdot}CS{\cdot}SH,NH_2R$$
$$2R_2NH+CS_2 \rightarrow R_2N{\cdot}CS{\cdot}SH,NHR_2$$

When the product from a *primary* amine is boiled with mercuric chloride, a metallic derivative of the alkyldithiocarbamic acid is produced, which decomposes into an alkyl*iso*thiocyanate (a *mustard oil*), an insoluble oil with a sharp smell (Hofmann's mustard-oil reaction) :

$$RNH{\cdot}CS_2HgCl \rightarrow HgS+HCl+RNCS$$

Tertiary bases do not react with carbon disulphide.

Aromatic primary bases readily yield *symm*-diarylthioureas, *e.g.* aniline gives thiocarbanilide :

$$2PhNH_2+CS_2 \rightarrow H_2S+SC(NHPh)_2$$

8. *With diethyl oxalate.*

Simple aliphatic primary and secondary bases react in the anhydrous state with diethyl oxalate, the former giving solid, water-soluble diamides, $RNH{\cdot}CO{\cdot}CO{\cdot}NHR$, and the latter liquid, water-insoluble oxamic esters,

$$R_2N{\cdot}CO{\cdot}CO_2Et,$$

and these compounds are decomposed by heating with aqueous alkalis, the amines being regenerated. Tertiary amines do not react. This reaction was used by A. W. Hofmann (Ber. 1870, **3**, 109, 776 ; O. Wallach, Ber. 1875, **8**, 760 ; *see also* Duvillier and Buisine, Ann. Chim. Phys. 1881 [v], **23**, 299) for the separation of the three ethylamines, and it has been used since in other cases.

9. *With the alkali metals.*

Metallic potassium reacts with primary and secondary bases with formation of substances of the types $RNHK$, RNK_2, or R_2NK. Metallic sodium reacts less readily. Such compounds are more readily formed in the aromatic than in the aliphatic series, *e.g.* diphenylamine prepared from the potassium derivative of aniline by reaction with bromobenzene. Carbazole is sufficiently acidic to form potassium carbazole with potassium hydroxide.

10. *With oxidising agents.*

The aliphatic amines are readily attacked by powerful oxidising agents, such as potassium permanganate, particularly in alkaline solution, when profound degradation occurs (*see* Vorländer, Annalen, 1906, **345**, 251).

With Caro's acid (H_2SO_5) primary aliphatic amines are oxidised to hydroxamic acids, $RC(OH){:}N{\cdot}OH$, ketoximes, $R_2C{:}N{\cdot}OH$, or nitroso-paraffins, $R_3C{\cdot}N{:}O$, according as the alkyl radical is primary, secondary, or tertiary.

Hydrogen peroxide reacts with primary aliphatic amines in the presence of ferrous sulphate to give the corresponding aldehydes (K. Suto, Biochem. Z. 1915, **71**, 169). Secondary amines react with hydrogen peroxide to give dialkylhydroxylamines, $R_2N{\cdot}OH$, and tertiary amines give the hydrates of the amine oxides, $[R_3NOH]OH$, which lose water on heating to form the amine oxides, $R_3N{\rightarrow}O$. The amine oxides combine with acids and alkyl halides to form salts of the types $[R_3NOH]Cl$ and $[R_3NOMe]I$ (for a proof of the unique character of the fifth valency of nitrogen based on these reactions, *see* Meisenheimer, Annalen, 1913, **397**, 273).

Aniline is oxidised by Caro's acid to nitrosobenzene and other products. Regulated oxidation of aniline with chromic acid yields *p*-benzoquinone as the final product. A large number of substances has been isolated as oxidation products of aniline, β-phenylhydroxylamine, nitrobenzene, azobenzene, azoxybenzene, nitrosobenzene, aniline black, etc., and a discussion of the subject is beyond the scope of this article ; reference may be made to S. Goldschmidt, Ber. 1920, **53** [B], 36 ; S. Goldschmidt and B. Wurzschmitt, Ber. 1922, **55** [B], 3223.

11. *With hypochlorous acid, etc.*

Primary and secondary aliphatic amines react with the halogens in the presence of alkali to give substances such as methyldichloroamine, $CH_3{\cdot}NCl_2$, or propylchloramine, $C_3H_7{\cdot}NHCl$. They are explosive compounds but less so than the nitrogen trihalides, and many of them can be distilled. Hydrolysis with weak acids regenerates the bases and gives, for example, hypochlorous acid ; concentrated hydrochloric acid gives the original base and chlorine, the acid behaving as a reducing agent.

An ethereal solution of hypochlorous acid at −20° reacts with aniline to give phenyldichloramine, $Ph{\cdot}NCl_2$, as an explosive yellow oil (S. Goldschmidt, Ber. 1913, **46**, 2728). The dichloramines derived from the nitranilines or pentachloraniline are crystalline and much more stable (*idem.* Ber. 1922, **55**, 2450). The action of hypochlorous acid on acetanilide readily gives *N*-chloracetanilide as a fairly stable compound, which is converted by hydrogen chloride in acetic acid into *p*-chloracetanilide. A similar compound is " Chloramine-T,"

$$p\text{-}CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NClNa,$$

which has found considerable application as an antiseptic, as it is readily hydrolysed yielding hypochlorous acid.

Tertiary aliphatic amines react with hypochlorous acid to give a dialkylchloramine, R_2NCl, with elimination of an alkyl group (Meisenheimer, Ber. 1913, **46**, 1148).

12. *With o-xylylene bromide.*

Primary amines react with *o*-xylylene bromide, giving liquid derivatives of dihydro-*iso*indole :

$$C_6H_4(CH_2Br)_2+NH_2R \rightarrow C_6H_4(CH_2)_2NR+2HBr$$

Secondary amines give crystalline quaternary ammonium bromides :

$$C_6H_4(CH_2Br)_2+NHRR' \rightarrow [C_6H_4(CH_2)_2NRR']Br+HBr$$

Tertiary aliphatic amines give addition products of one molecule of xylylene bromide with two of the amine. Tertiary amines containing one or more aromatic nuclei do not react (Scholtz, Ber. 1898, **31**, 1707).

13. *Dealkylation of bases.*

Secondary, tertiary, and quaternary ammonium bases can be dealkylated by distilling their dry hydrochlorides, when they lose a molecule of alkyl halide (usually methyl chloride if a methyl group is present) :

$$[(CH_3)_3NH]Cl \rightarrow (CH_3)_2NH+CH_3Cl$$

The reaction can sometimes be carried out with concentrated hydrochloric acid at 200°–300°.

Tertiary bases can be made to yield secondary bases by loss of their smallest alkyl group by treatment with cyanogen bromide (von Braun, Ber. 1900, **33**, 1438 ; 1910, **43**, 3209), and subsequent hydrolysis of the intermediate dialkylcyanamide with 30% sulphuric acid :

$$R_3N+CNBr \rightarrow [R_3N{\cdot}CN]Br \rightarrow R_2N{\cdot}CN+RBr$$

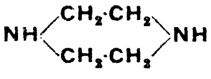
ALIPHATIC DIAMINES, ETC.

The aliphatic diamines may be regarded as derived from hydrocarbons by replacement of two hydrogen atoms by two amino-groups. The most important are the ω-diamines of the normal paraffin hydrocarbons, $NH_2{\cdot}[CH_2]_n{\cdot}NH_2$, certain of which are produced by the putrefaction of animal matter, *e.g.* putrescine (tetramethylenediamine) and cadaverine (pentamethylenediamine). They arise from the two diamino-acids ornithine, $NH_2{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2H$, and lysine, $NH_2[CH_2]_4{\cdot}CH(NH)_2{\cdot}CO_2H$, by loss of carbon dioxide, the amino-acids themselves being hydrolysis products of proteins. The diamino-carboxylic acids also lose carbon dioxide on distillation (*see* art. AMINO-ACIDS).

Preparation.—The methods are analogous to those used in the preparation of monamines, and only brief mention will be made of them. (1) By heating alkylene dibromides with alcoholic ammonia at 100°, *e.g.* ethylene dibromide gives ethylene diamine,

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

accompanied by diethylenediamine (piperazine),



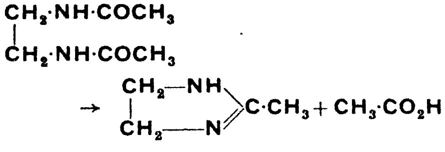
In this reaction the yield of the simple diamine is increased by carrying out the reaction in the presence of zinc chloride or cupric chloride or other substance capable of forming a complex metallic derivative. (2) By reduction of dicyanides, dioximes, and dihydrazones of dialdehydes or diketones, or dinitroparaffins. (3) From dicarboxylic acids through the Hofmann or Curtius degradations. (4) By hydrolysis of alkylenediphthalimides (Gabriel).

Properties.—The polymethylenediamines are volatile liquids or solids of low melting-point, and the melting-points of the members of the homologous series show alternation like those of the dibasic acids (the melting-points of some of the homologues are as follows, C_2, etc., indicating the number of methylene groups : C_2, 8·5° ; C_3, liquid ; C_4, 27° ; C_5, liquid ; C_6, 42° ; C_7, 29° ; C_8, 51° ; C_9, 37° ; C_{10}, 62°. They possess ammoniacal odours, are easily soluble in water, with which they form hydrates of considerable stability (compare hydrazine), and absorb carbon dioxide from the air. They are powerful di-acid bases. When shaken with benzoyl chloride and aqueous alkali they yield dibenzoyl derivatives, and with phenyl*iso*cyanate they give ureas,

$$[CH_2]_n{\cdot}(NH{\cdot}CO{\cdot}NHPh)_2,$$

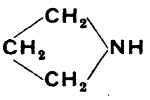
both of these types of derivative serve to identify the diamines.

Aliphatic diamines give the ordinary reactions characteristic of the amino-group, but frequently also possess the property of forming condensation products containing nitrogen rings. Thus the diacetyl derivative of ethylenediamine when heated above its melting-point yields a derivative of iminazole :

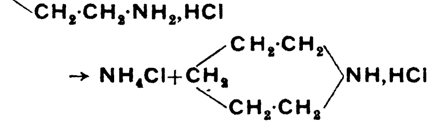


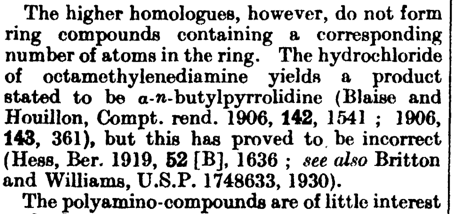
and similar compounds are produced in the case of the diacetyl derivatives of tri- and tetramethylene diamines.

Cyclic compounds are also produced by distilling the dihydrochlorides of the aliphatic diamines, the nature of the product depending upon the number of carbon atoms separating the amino-groups. Thus ethylenediamine yields piperazine ; trimethylene diamine gives a very poor yield of *cyclo*trimethyleneimine,



tetra- and penta-methylenediamine give good yields of pyrrolidine and piperidine respectively :





The higher homologues, however, do not form ring compounds containing a corresponding number of atoms in the ring. The hydrochloride of octamethylenediamine yields a product stated to be α-*n*-butylpyrrolidine (Blaise and Houillon, Compt. rend. 1906, **142**, 1541 ; 1906, **143**, 361), but this has proved to be incorrect (Hess, Ber. 1919, **52** [B], 1636 ; *see also* Britton and Williams, U.S.P. 1748633, 1930).

The polyamino-compounds are of little interest with the exception of *spermine*, a tetra-amino derivative of the constitution

$$NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2,$$

first isolated from human semen by Schreiner, and occurring in many mammalian organs (*see* H. W. Dudley, M. C. Rosenheim, and O. Rosenheim, Biochem. J. 1924, **18**, 1263 ; Dudley, O. Rosenheim, and W. W. Starling, *ibid.* 1926, **20**, 1082).

AROMATIC DIAMINES, ETC.

Aromatic diamines are usually prepared either by the reduction of dinitro-compounds or of nitroamino-compounds with tin or stannous chloride and hydrochloric acid, or by the reduction of aminoazo-compounds :

$$NH_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_5+4[H] \rightarrow NH_2\cdot C_6H_4\cdot NH_2+NH_2\cdot C_6H_5$$

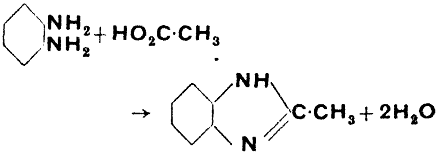
p-Phenylenediamine may be prepared by the action of ammonia upon *p*-chloroaniline in presence of copper salts (G.P. 204848, 1908).

They are colourless, crystalline substances, easily soluble in water and very readily oxidised in solution. They yield stable salts with two equivalents of acid. The chemical behaviour of the diamines depends largely on the relative positions of the two amino-groups. The *o*-diamines, unlike the *m*- and *p*-diamines, readily form cyclic compounds.

Reactions.

1. *With organic acids.*

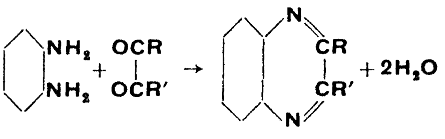
o-Diamines react with anhydrous carboxylic acids yielding benziminazoles (benzoglyoxalines) :



The benziminazoles are basic substances, and are, therefore, easily distinguished from the diamides, $C_6H_4(NH\cdot CO\cdot CH_3)_2$, which are formed by the interaction of *m*- and *p*-diamines with acids. *o*-Diamines react with acid anhydrides to form the diamides, but when heated these yield the acid and the benziminazole.

2. *With* 1 : 2-*dicarbonyl compounds.*

o-Diamines condense readily with 1 : 2-dicarbonyl compounds to give derivatives of quinoxaline (Hinsberg, Annalen, 1887, **237**, 327) :

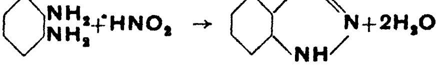


and use is made of this type of reaction for their identification. The *o*-diamine is condensed in acetic acid or alcoholic solution with phenanthraquinone, when the very sparingly soluble phenanthrazine separates.

No analogous reactions occur in the case of the *m*- and *p*-diamines.

3. *With nitrous acid.*

o-Diamines when treated with nitrous acid yield benzotriazoles (aziminobenzenes) :



as extremely stable, non-basic, crystalline substances, which are unaffected by boiling with acids or alkalis.

m-Diamines react with nitrous acid under ordinary conditions to give brown aminoazo dyes, formed by the diazonium salt coupling with the undiazotised base. In the case of *m*-phenylenediamine itself the product is known as Bismarck Brown, and consists of a mixture of aminoazo compounds, of which the simplest is 3 : 2′ : 4′-triaminoazobenzene,

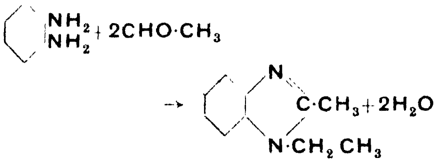
$$NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$$

The formation of Bismarck Brown is used in water analysis as a test for the presence of nitrites. *m*-Diamines may be tetrazotised in strongly acid solution in presence of excess of nitrous acid.

p-Diamines react normally with nitrous acid in presence of mineral acid and undergo tetrazotisation.

4. *With aldehydes, etc.*

o-Diamines react with aldehydes, such as acetaldehyde, giving *aldehydines*, which are alkylated benziminazoles :

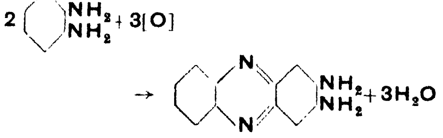


m- and *p*-Diamines react with aldehydes to give dialkylidene derivatives.

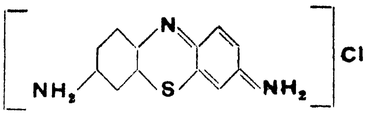
With the following reagents *o*-diamines, as distinct from *m*- and *p*-diamines, give heterocyclic compounds : sulphur dioxide (gives piazothiole), carbonyl chloride (*o*-phenyleneureas), cyanogen (diaminoquinoxalines), catechol (phenazines), ethylene dibromide (tetrahydroquinoxalines), oxalic acid (dihydroxyquinoxalines), phthalic anhydride (benzimidazol-2-phenyl-*o*-carboxylic acids).

5. *With oxidising agents.*

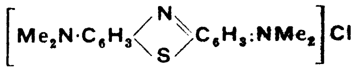
Acid solutions of *o*-phenylenediamine are coloured deep red by the addition of ferric chloride owing to the formation of the hydrochloride of diaminophenazine :



p-Phenylenediamine is oxidised by manganese dioxide and sulphuric acid, or by ferric chloride, to *p*-benzoquinone. When a *p*-diamine is oxidised in presence of an aromatic monamine, or a phenol, a dyestuff of the indamine or indophenol class is produced ; at higher temperatures the products are safranines (*q.v.*). *p*-Diamines containing one free amino-group are oxidised by ferric chloride in aqueous solution of hydrogen sulphide to form dyestuffs of the phenothiazine group ; *p*-phenylenediamine itself yields Lauth's Violet,



The important dyestuff Methylene Blue is the corresponding compound prepared from *asym*-dimethyl-*p*-phenylenediamine,



$$\left[Me_2N{\cdot}C_6H_3{<}\begin{matrix}N\\S\end{matrix}{>}C_6H_3{:}NMe_2\right]Cl$$

The more important homologues of the simple diamines are 2 : 4-diaminotoluene prepared by the reduction of 2 : 4-dinitrotoluene ; 2 : 5-diaminotoluene prepared by reducing nitro-*o*-toluidine ; 3 : 4-diaminotoluene prepared from acet *p*-toluidide by nitration, reduction, and hydrolysis.

Triaminobenzenes are of little importance. 1 : 3 : 5-Triaminobenzene is prepared as the hydrochloride by reducing 1 : 3 : 5-trinitrobenzene, and when the hydrochloride is boiled with water all three amino-groups are hydrolysed with production of phloroglucinol and ammonium chloride. This facility for hydrolysis is shared by other compounds possessing *m*-amino-groups. Tri- and tetra-aminobenzenes are considerably less stable than the diaminobenzenes, and penta-aminobenzene decomposes in water almost instantaneously, although its trihydrochloride shows greater stability. Penta-aminobenzene and hexa-aminobenzene may be easily prepared by the method of Flürscheim and Holmes (J.C.S. 1929, 330) from polynitroaminobenzenes by reduction with phenylhydrazine at 120°–200°. Penta-aminobenzene is also prepared from *m*-nitraniline *via* the stages tetranitroaniline, trinitrodiaminobenzene, and final reduction with phenylhydrazine. Hexa-aminobenzene is available from 1 : 3 : 5-trinitrobenzene through the stages 3 : 5-dinitroaniline, pentanitroaniline, trinitrotriaminobenzene, and final reduction with phenylhydrazine. In contrast with the other polyaminobenzenes, hexa-aminobenzene shows remarkable stability. It is a solid melting with decomposition at 247°–248°, stable in the solid state, and decomposes only slowly in aqueous solution. It is insoluble in all organic solvents with the exception of phenylhydrazine. It forms a hexa-acetyl derivative, a tetrahydrochloride, and a tripicrate. Trinitrotriaminobenzene cannot be reduced by ordinary reducing agents; either decomposition occurs or the product is penta-aminobenzene (Palmer and Jackson, Ber. 1888, 21, 1706 ; Palmer and Grindley, *ibid.* 1893, 26, 2304). W. B.

AMINO-ACIDS. By custom the term amino-acid indicates membership of a large group of compounds which are simultaneously aliphatic primary amines and aliphatic carboxylic acids, although it is clear that in strict parlance the name should be applicable to any substance, aliphatic, aromatic, or heterocyclic, which is both a nitrogenous base and an acid, carboxylic or otherwise. Heterocyclic acids and aromatic amino-acids, such as the amino-benzoic acids, are however more suitably discussed under their respective titles, and attention is now focused on those amino-acids which occur in the free state in the tissues of plants and animals or are combined in the proteins (*q.v.*) and in the products of their partial degradation, proteoses, peptones, and polypeptides. With few exceptions these amino-acids contain a primary amino-group and a carboxyl group attached to the same carbon atom, and are therefore α-amino-acids. Vickery and Schmidt (Chem. Rev. 1931, **9**, 169) describe the history of twenty-one amino-acids and include a section on amino-acids the existence of which is less firmly established. Reviews of recent progress will be found in Ann. Rev. Biochem. 1932, **1**, 151 ; 1933, **2**, 71 ; 1934, **3**, 111 ; 1935, **4**, 93.

Classification and Individual Amino-Acids.

The amino-acids are classified according to the number of basic and acidic groups which they contain.

(1) Monoamino-monocarboxylic acids (neutral).

(2) Diamino-monocarboxylic acids (basic).

(3) Monoamino-dicarboxylic acids (acidic).

(4) Imino-acids (neutral).

Monoamino-monocarboxylic acids.

Glycine,* $NH_2\cdot CH_2\cdot CO_2H$.

d-Alanine,* $NH_2\cdot CHMe\cdot CO_2H$.

l-Serine,* $CH_2(OH)\cdot CH(NH_2)CO_2H$.

d-Aminobutyric acid,
$CH_2Me\cdot CH(NH_2)CO_2H$.

d-Valine,* $CHMe_2\cdot CH(NH_2)CO_2H$.

d-Norvaline,* $CH_2Me\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-Leucine,* $Me_2CH\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-*iso*Leucine, $MeEtCH\cdot CH(NH_2)CO_2H$.

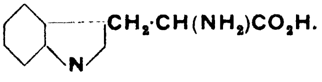
d-Norleucine,*
$CH_2Me\cdot CH_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-Phenylalanine,* $CH_2Ph\cdot CH(NH_2)CO_2H$.

l-Tyrosine,*
$(p)HO\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-3 : 4-Dihydroxyphenylalanine,
$(HO)_2C_6H_3\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-Tryptophane,*



l-Cysteine,* $HS\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-Cystine,*
$CO_2H\cdot CH(NH_2)CH_2\cdot S\cdot S\cdot CH_2$
$\cdot CH(NH_2)CO_2H$.

l-Methionine,*
$MeS\cdot CH_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-3 : 5-Diiodotyrosine,
$I_2(OH)C_6H_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

l-Thyroxine,*
$HO\cdot C_6H_2I_2\cdot O\cdot C_6H_2I_2\cdot CH_2$
$\cdot CH(NH_2)CO_2H$.

Diamino-monocarboxylic acids.

d-Arginine,*
$NH_2\cdot C(:NH)NH\cdot CH_2\cdot CH_2\cdot CH_2$
$\cdot CH(NH_2)CO_2H$.

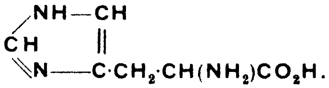
d-Ornithine,*
$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-Citrulline,
$NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2$
$\cdot CH(NH_2)CO_2H$.

d-Lysine,*
$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-Canavanine,
$NH_2\cdot C(:NH)\cdot NH\cdot O\cdot CH_2\cdot CH_2$
$\cdot CH(NH_2)CO_2H$.

l-Histidine,*



Monoamino-dicarboxylic acids.

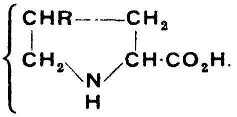
d-Aspartic acid,*
$CO_2H\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-Glutamic acid,*
$CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH_2)CO_2H$.

d-β-Hydroxyglutamic acid,
$CO_2H\cdot CH_2\cdot CH(OH)CH(NH_2)CO_2H$.

Imino-acids.

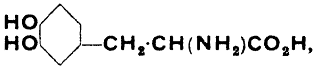
l-Proline,* R = H.
l-Hydroxy-* proline, R = OH



Amino-acids marked * are described in separate articles (*q.v.*) and the following are brief accounts of other important members of the group.

d-*iso*-Leucine, $MeEtCH\cdot CH(NH_2)CO_2H$. Discovered by Ehrlich (Z. Ver. deut. Zucker-Ind. 1903, 809) and synthesised by him (Ber. 1908, **41**, 1453), occurs uncombined in seedlings and in beet molasses, while *l*(+)-*iso*-leucine is found in brain tissue (Abderhalden and Beckmann, Z. physiol. Chem. 1932, **207**, 93). It has m.p. in sealed tube 284° when heated quickly, but sublimes in open tube at 230° ; it is more soluble in water than leucine, and moderately soluble in hot methyl alcohol. It has $[\alpha]_D$ in water, +9·6° (Ehrlich, Ber. 1904, **37**, 1809), +11·3° (Locquin, Bull. Soc. chim. 1907 [iv], **1**, 601) ; in 20% HCl, +36·8° (Ehrlich, *l.c.*), +34·3° (Levene and Jacobs, Biochem. Z. 1908, **9**, 231), +41·3° (Abderhalden, Hirsch, and Schuler, Ber. 1909, **42**, 3394), +40·6° (Locquin, *l.c.*) ; in dilute alkali, +11·1° (Ehrlich, *l.c.*). Hot baryta converts it into *d*-*allo*-*iso*leucine by stereoisomeric change. Abderhalden and Zeisset (Z. physiol. Chem. 1931, **195**, 121) resolved synthetic leucine into *l*(+)- and *d*(−)-*iso*leucines and *d*(−)- and *l*(+)-*allo*-*iso*leucines. *d*-*iso*Leucine is converted into *d*-amyl alcohol, an important constituent of fusel oil, by yeast fermenting in presence of sugar.

l-3 : 4-Dihydroxyphenylalanine, (*Dopa*),



m.p. 282°; isolated from vetch seedlings (Torquati Chem. Zentr. 1913, II, 517, 518), pods of the broad bean (Guggenheim, Z. physiol. Chem. 1913, **88**, 276), and Georgia velvet bean (Miller, J. Biol. Chem. 1920, **44**, 481). Not yet found in the animal body. Constitution determined by Guggenheim (Z. physiol. Chem. 1913, **88**, 276). *d*- and *l*-isomers synthesised by Harington and Randall (Biochem. J. 1931, **25**, 1028) and *dl*-compound by Funk (J.C.S. 1911,

99, 554 ; Stephen and Weizmann, J.C.S. 1914, **105**, 1152 ; Hirai, Biochem. Z. 1921, **114**, 67 ; Sugii, J. Pharm. Soc. Japan, 1921, **130**, 136 ; Harington and McCartney, Biochem. J. 1927, **21**, 852 ; Harington, Biochem. J. 1928, **22**, 407). Moderately soluble in water, insoluble in alcohol. Readily oxidised in alkaline solution by air, and by ammoniacal silver nitrate solution. $[\alpha]_D^{20}$ $-12{\cdot}0°$ in *N*-HCl. Configuration corresponds to that of *d*-alanine (Karrer and Kehl, Helv. Chim. Acta, 1930, **13**, 50). For estimation, alone and in presence of tyrosine, *see* Pincussen and Hammerich (Biochem. Z. 1931, **239**, 273). Dissociation constants (Miyamoto and Schmidt, J. Biol. Chem. 1931, **90**, 165). Dopa is formed from tyrosine as the first stage in the oxidation of tyrosine to melanin by tyrosinase (Onslow and Robinson, Biochem. J. 1925, **19**, 420 ; Raper, Biochem. J. 1926, **20**, 735), and the corresponding reaction *in vitro*, the progressive oxidation of phenylalanine by hydrogen peroxide to tyrosine and then to dihydroxyphenylalanine, is recorded by Raper (Biochem. J. 1932, **26**, 2000). This formation from tyrosine links up the formation of adrenaline from tyrosine (Raper, Biochem. J. 1927, **21**, 89), since Bloch (Z. physiol. Chem. 1917, **98**, 226), Bloch and Schaaf (Biochem. Z. 1925, **162**, 181 ; Klin. Woch. 1932, **11**, 10), and Peck, Sobotka, and Kahn (Klin. Woch. 1932, **11**, 14) find that dopa is the only effective substrate for the production of melanin by the dopa-oxidase of epithelial cells, although such an enzyme has not yet been found in the adrenal gland.

Citrulline,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

m.p. 220°–222°, found by Wada (Biochem. Z. 1930, **224**, 420) in the free state in the juice of water melons and isolated by him (Biochem. Z. 1933, **257**, 1) from a tryptic digest of caseinogen. It occurs free and combined in the seeds of a variety of plants, is stable to hot hydrochloric acid but is readily decomposed by alkali to give ammonia and ornithine. It was synthesised from ornithine by Wada (Biochem. Z. 1930, **224**, 420), is soluble in water, insoluble in alcohol, neutral to litmus. It is precipitated by phosphotungstic acid and mercury salts in alkaline solution, but not by phosphomolybdic acid, tannic acid or basic lead acetate. It accompanies arginine and ornithine in the hexone base fraction of amino-acid fractionations, and examples of its isolation and separation from hexone bases are given by Winterstein ("Handbuch der Pflanzenanalyse," 1933, **4**, 63, Springer, Vienna). Putrefactive bacteria convert arginine into citrulline (Ackermann, Z. physiol. Chem. 1931, **203**, 66), but this change has not yet been observed in animals (Ackermann, Z. physiol. Chem. 1932, **209**, 12). According to modern theories of urea formation in plants and animals citrulline plays an important part as an intermediate (Krebs and Henseleit, Z. physiol. Chem. 1932, **210**, 33 ; Krebs, Ergebn. Enzymforsch. 1934, **3**, 247).

Canavanine,

$$NH_2{\cdot}C(:NH)NH{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

m.p. 184°, was isolated from jackbean meal by Kitagawa and collaborators (J. Biochem. Japan, 1929, **11**, 265 ; Proc. Imp. Acad. Japan, 1929, **5**, 380) and by Gulland and Morris (J.C.S. 1935, **763**). The constitution was determined by Gulland and Morris (*l.c.*) and Kitagawa and Yamada (J. Biochem. Japan, 1932, **16**, 339). Yields canaline,

$$CH_2(ONH_2){\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

and urea by fission with canavanase of liver (Kitagawa and Monobe, J. Biochem. Japan, 1933, **18**, 333). $[\alpha]_D^{20}$ $+8{\cdot}09$ in water. It is soluble in water and hot alcohol ; for dissociation constants, *see* Tomiyama (J. Biol. Chem. 1935, **111**, 45). It does not give the Sakaguchi reaction for arginine, but gives a reddish-purple colour with irradiated sodium nitroprusside solution.

β-Hydroxyglutamic acid,

$$CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO_2H,$$

loses water of crystallisation at about 110° and melts at 130°–135° ; was isolated in crystalline state from caseinogen, glutenin, gliadin, and zein by Dakin (Biochem. J. 1918, **12**, 303 ; 1919, **13**, 424 ; Z. physiol. Chem. 1923, **130**, 159) and from caseinogen by Gulland and Morris (J.C.S. 1934, 1644). It is oxidised to malic semialdehyde by chloramine-T, is soluble in water and glacial acetic acid and is feebly dextrorotatory in aqueous solution. Optically inactive forms (2 asymmetric carbon atoms) have been synthesised by Dakin (Biochem. J. 1919, **13**, 398) and by Harington and Randall (Biochem. J. 1931, **25**, 1917). Dissociation constants of the synthetic acid were determined by Richardson (Biochem. J. 1931, **25**, 1925).

PROPERTIES, REACTIONS, AND DERIVATIVES.

The amino-acids are colourless, crystalline solids which melt with decomposition (*see* Dunn and Brophy, J. Biol. Chem. 1932, **99**, 221, for determination of decomposition temperatures). They usually dissolve readily in water (Dalton and Schmidt, J. Biol. Chem. 1933, **103**, 549 ; Dunn, Ross, and Read, J. Biol. Chem. 1933, **103**, 579) and are sparingly soluble in alcohol, although there are several exceptions to this generalisation, *e.g.* cystine is very sparingly soluble in water, proline dissolves readily in alcohol. They do not dissolve in non-ionising solvents. (For summary of the factors concerned in the solubilities of amino-acids, *see* Cohn, Naturwiss. 1932, **20**, 663).

By possession of both carboxyl and amino-groups, the amino-acids are capable of forming a large variety of derivatives, some related to each group separately, others formed from both groups simultaneously. These derivatives are important in the detection of the presence or absence of certain amino-acids in mixtures ; in removing certain amino-acids from solution ; in the isolation, purification, and characterisation of the individual acids ; and in their quantitative determination. Mitchell and Hamilton ("Biochemistry of the Amino-acids," 1929, p. 34, Chemical Catalog Co., New York) give a bibliography of the characteristic derivatives of most of the amino-acids. The carboxyl groups of amino-acids enter into all the reactions characteristic of the group, *e.g.* salt formation with metals (Abderhalden, "Biochemisches Handlexicon," Vol. 4, 1911, Berlin) and with organic bases; combination with alcohols to form esters, formation of amino-acid chloride hydrochlorides, $[\mathrm{RCH(NH_3)COCl}]^+\mathrm{Cl}^-$, and of acylated amino-acid chlorides (Fischer, Ber. 1905, **38**, 605). By virtue of their amino-groups the amino-acids form salts with acids, may be acylated, and undergo the other reactions characteristic of the aliphatic amino-group. Masking of either the acidic or basic function yields compounds which exhibit to an enhanced degree the properties of the residual group. The basic nature of the amino-group increases with increasing distance from the carboxyl group along the carbon chain (Orthner and Hein, Biochem. Z. 1933, **262**, 461).

Esters (Fischer, Ber. 1906, **39**, 530; Abderhalden, Handbuch der biochem. Arbeitsmethoden, 1910, **2**, 475). The ester hydrochlorides are formed by the interaction of dry methyl or ethyl alcohols with the amino-acids in presence of hydrogen chloride. The free esters are liberated by means of silver oxide or cold sodium hydroxide solution and are basic liquids or solids, which dissolve in non-ionising solvents and are readily hydrolysed to the amino-acids.

Copper salts (Winterstein, "Handbuch der Pflanzenanalyse," 1933, **4**, 21, Springer, Vienna) are prepared by heating aqueous solutions of the amino-acids with copper hydroxide or carbonate, or by the action of cupric acetate. The concentration of metallic ions in solutions of the nickel, cobalt and cupric salts is low (Ley, Z. anorg. Chem. 1927, **164**, 377) owing to chelate-ring formation between the metallic and amino-groups (Sidgwick, "Electronic Theory of Valency," 1927, 245, Oxford University Press). The solubilities of copper salts vary considerably in the case of different amino-acids, and Brazier (Biochem. J. 1930, **24**, 1188) has based a method of separation of amino-acids on the relative solubilities of their copper salts.

Salts with acids.—The acids used in the preparation of sparingly soluble salts for isolation, purification, or characterisation are: hydrochloric, nitric, sulphuric, oxalic, picric (tabular summary, Winterstein, "Handbuch der Pflanzenanalyse, 1933, **4**, 22); picrolonic (Steudel, Z. physiol. Chem. 1903, **37**, 219; Mayeda, Z. physiol. Chem. 1907, **51**, 261; Abderhalden and Weil, Z. physiol. Chem. 1912, **78**, 150; Levene and Van Slyke, J. Biol. Chem. 1912, **12**, 127; tabular summary, Winterstein, "Handbuch der Pflanzenanalyse," 1933, **4**, 24); flavianic (Kossel and Gross, Z. physiol. Chem. 1924, **135**, 167; Langley and Albrecht, J. Biol. Chem. 1935, **108**, 729); rufianic (Zimmermann, Z. physiol. Chem. 1930, **188**, 180; Gulland and Morris, J.C.S. 1935, 763); sozoiodolic (2 : 6-di-iodophenol-4-sulphonic) (Ackermann, Z. physiol. Chem. 1934, **225**, 46); Reinecke's (Kapfhammer and Eck, Z. physiol. Chem. 1927, **170**, 294; Kapfhammer and Spörer, Z. physiol. Chem. 1928, **173**, 245; Grassmann and Lang, Biochem. Z. 1934, **269**, 223); rhodanilic (Bergmann, J. Biol. Chem. 1935, **110**, 471); chloroplatinic, chloroauric, phosphotungstic (for examples and literature, *see* Drummond, Biochem. J. 1918, **12**, 5; Thimann, Biochem. J. 1930, **24**, 368; Peters, Biochem. J. 1930, **24**, 1852); phosphomolybdic; for the use of "permutite" for the separation of certain amino-acids from solution, *see* Whitehorn, J. Biol. Chem. 1923, **56**, 751; Sadikov and Lindkvist-Risakova, A. 1934, 727.

Complex salts.—The amino-acids form complex salts with the salts of metals such as silver, mercury, lead, copper, cadmium, zinc, barium, calcium, lithium, sodium, potassium, etc. These compounds may be insoluble, in which case they find extensive use for separations. Mercuric acetate in presence of sodium carbonate is especially valuable as a precipitant (Neuberg and Kerb, Biochem. Z. 1912, **40**, 498; 1914, **67**, 119), and Vickery and Gordon (J. Biol. Chem. 1933, **103**, 543) have studied the best conditions as regards molecular equivalents of mercuric chloride, alkali, p_H and volume of alcohol added for the precipitation of amino-acids as complexes with mercuric chloride. Alternatively the complexes may be soluble, and then the properties of the amino-acids (*e g.* solubilities, optical rotations, etc.) may be profoundly modified (Pfeiffer, "Organische Molekularverbindungen," 1927, Enke, Stuttgart; Clough, J.C.S. 1918, **113**, 526; King and Palmer, Biochem. J. 1920, **14**, 574; Joseph, J. Biol. Chem. 1935, **111**, 479, 489). Cryoscopic and refractometric measurements of solutions of pairs of amino-acids show that double compounds are formed, and the isolation of some of these is recorded (Frankel, Biochem. J. 1931, **242**, 67).

Acyl derivatives.—The following acyl derivatives in general use are prepared as indicated below and are usually hydrolysed by hot mineral acids.

Formyl, prepared by repeatedly heating the amino-acids with anhydrous formic acid (Fischer and Warburg, Ber. 1905, **38**, 3998), or, more rapidly, by continuous removal of the water formed by distilling the mixture with toluene (Steiger, J. Biol. Chem. 1930, **86**, 695).

Acetyl, prepared by the action of acetyl chloride in a basic organic solvent, by the action of ketene on the amino-acid (Bergmann and Stern, Ber. 1930, **63**, 437) and by the action of acetic anhydride (1 mol.) (Knoop and Blanco, Z. physiol. Chem. 1925, **146**, 267). Excess of acetic anhydride causes racemisation at the α-carbon atom (Bergmann and Zervas, Biochem. Z. 1928, **203**, 280; du Vigneaud and Meyer, J. Biol. Chem. 1932, **98**, 295; **99**, 143; Csonka and Nicolet, J. Biol. Chem. 1932, **99**, 580). Vigorous acetylation by hot acetic anhydride and pyridine decarboxylates α-amino-acids, acetylates the amino-group and introduces an acetyl group on the α-carbon atom; phenyl alanine, for example, yields acetylamino-benzyl-acetone (Dakin and West, J. Biol. Chem. 1928, **78**, 91, 745). Prolonged acetylation with hot acetyl chloride converts amino-acids into oxazoles (Wrede and Feuerriegel, Z. physiol. Chem. 1933, **218**, 129).

Benzoyl (table, Winterstein, "Handbuch der Pflanzenanalyse," 1933, **4**, 25), p-*nitrobenzoyl*, and 3 : 5-*dinitrobenzoyl*, prepared by the Schotten-Baumann reaction, best in bicarbonate solution (Fischer, Ber. 1899, **32**, 2453 ; Fischer and Jacobs, Ber. 1906, **39**, 2942) or in pyridine.

p-Toluenesulphonyl (Fischer and Bergmann, Annalen, 1913, **398**, 117 ; Z. physiol. Chem. 1914, **89**, 158 ; Ber. 1915, **48**, 360).

β-Naphthalenesulphonyl (Fischer and Bergel, Ber. 1902, **35**, 3779 ; table, Winterstein, "Handbuch der Pflanzenanalyse," 1933, **4**, 28, 30).

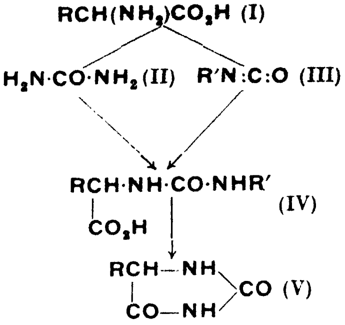
4-*Nitrotoluene*-2-*sulphonyl* (Siegfried, Z. physiol. Chem. 1904, **43**, 68 ; Oseki, Amer. Chem. Abstr. 1920, **14**, 2780), prepared by shaking an ethereal solution of the acid chloride with an alkaline, aqueous solution of the amino-acid.

Benzylcarbonyl, Ph·CH$_2$·O·CO·, prepared by the Schotten-Baumann method using benzylcarbonyl chloride (Bergmann and Zervas, Ber. 1932, **65** [B], 1192). Removal of the acyl group is effected by reduction with palladium black (Bergmann and Zervas, *l.c.*), with phosphonium iodide (Harington and Mead, Biochem. J. 1935, **29**, 1602), or with sodium in liquid ammonia (Loring and du Vigneaud, J. Biol. Chem. 1935, **111**, 385).

Condensation with aldehydes.—The undissociated amino-groups of amino-acid anions, *i.e.* amino-acids in alkaline solution, react with formaldehyde to give products of unknown constitution (Levy, J. Biol. Chem. 1933, **99**, 767 ; 1934, **105**, 157 ; 1935, **109**, 361, 365 ; Richardson, Proc. Roy. Soc. 1934, B, **115**, 121 ; Svehla, Ber. 1923, **56** [B], 331 ; Harris, Proc. Roy. Soc. 1929, B, **104**, 412 ; Biochem. J. 1930, **24**, 1080 ; Gróh and Hanák, Z. physiol. Chem. 1930, **190**, 169 ; Holden and Freeman, Austral. J. Exp. Biol. 1931, **8**, 189 ; Gubarev and Bystrenin, Biochem. Z. 1932, **255**, 92). According to Levy α-amino-acids react with 2 mols. and proline with 1 mol. of formaldehyde. The reactions are equilibria which depend chiefly on the concentration of the reagents and the p_H of the solutions, and they have received much attention owing to their importance in the Sørensen formol titration of amino-acids and proteins (Biochem. Z. 1907, **7**, 45) and in the study of zwitterions. For *N*-methylation and deamination by formaldehyde, *see* Clarke, Gillespie, and Weisshaus (J. Amer. Chem. Soc. 1933, **55**, 4571).

Some aromatic aldehydes react with amino-acids to yield compounds of the type of N-benzylidene-αβ-diphenylhydroxyethylamine (from benzaldehyde and glycine) (Erlenmeyer) or N-arylidene-amino-acids (Bergmann), the product depending on the conditions. Gulland and Mead (J.C.S. 1935, 210 ; bibliography) extended these results and showed that the equilibria involved depend on the concentration of the reactants, the p_H, and the nature of the aromatic aldehyde (*see also* Gulland and Mead, Biochem. J. 1935, **29**, 397).

Uramino-acids and hydantoins.—The α-amino-acids (I) react with urea (II) or with *iso*cyanates (III) (metallic or alkyl) to yield uramino-acids (IV), which pass under the influence of hot mineral acids into cyclic lactams, the hydantoins (V).



(R′ = alkyl or H)

Prolonged heating with acid or alkali is stated to convert hydantoins into amines by decarboxylation (*e.g.* phenylethylamine from phenylalanine, Wada, Biochem. Z. 1933, **260**, 47), but this is not confirmed by Clarke, Foster and Vickery, Biochem. Z. 1934, **272**, 376). Regeneration of the amino-acids is effected by hydrolysis with ammonia (Boyd and Robson, Biochem. J. 1935, **29**, 546). The uramino-acids and hydantoins are used to characterise amino-acids (Boyd, Biochem. J. 1933, **27**, 1838), the derivatives from phenyl- and α-naphthyl*iso*cyanates being in most general use (for tables, *see* Winterstein, "Handbuch der Pflanzenanalyse," 1933, **4**, 30–33). Uramino-acids and hydantoins have been found in the urine of animals which have been fed with amino-acids, and uramino-acids can easily be produced from urea and amino-acids in the concentration of urine by heat (Lippich, Ber. 1908, **41**, 2953, 2974 ; Dakin, J. Biol. Chem. 1910, **8**, 25).

Carbamino-acids.—The calcium or barium salts of α-amino-acids unite with carbon dioxide to form the corresponding salts of the carbamino acids (O·CO·CHR·NH·CO·O)Ba (Siegfried, Ergebn. Physiol. 1910, **9**, 334 ; Siegfried and Schutt, Z. physiol. Chem. 1912, **81**, 260 ; Buston and Schryver, Biochem. J. 1921, **15**, 636). These salts are precipitated from water or by the addition of alcohol, and the reaction may be used to separate amino-acids from other substances or from each other. The amino-acids are regenerated by heating the aqueous solutions of the carbamates, whereby barium carbonate is precipitated. It is probable that carbon dioxide is transported in the body partly in the form of carbamino-derivatives.

Deamination by nitrous acid.—Amino-acids are converted into hydroxy-acids when treated with nitrous acid :

$$NH_2\cdot CHR\cdot CO_2H + HNO_2 \rightarrow HO\cdot CHR\cdot CO_2H + N_2 + H_2O$$

The reaction is important, since it is the basis of the van Slyke method for determining the free amino-groups in amino-acids, proteins, and other substances (J. Biol. Chem. 1911, **9**, 185 ; 1911–12, **10**, 15 ; 1912, **12**, 275 ; 1913, **16**, 121 ; 1915, **23**, 407). The method is also used to follow the progress of the hydrolysis of proteins, which results in an increase of amino-groups (bibliography, Richardson, Proc. Roy. Soc. 1934 [B], **115**, 142, 162). α-Amino-groups react most rapidly, the rate decreasing as the distance between the amino- and the carboxyl-group increases (Dunn and Schmidt, J. Biol. Chem. 1922, **53**, 401 ; Plimmer, Biochem. J. 1924, **18**, 105 ; Hunter, J. Biol. Chem. 1929, **82**, 731). Secondary oxidation may produce errors in the estimation (bibliography, Richardson, *l.c.*). The principal reacting species are undissociated nitrous acid and the zwitterion-form (*see* p. 323) of the amino-acid (Taylor, J.C.S. 1928, 1897).

Grignard reagents (RMgX) convert amino-acid esters into amino-alcohols :

$$NH_2{\cdot}CHR'{\cdot}CO_2Et \rightarrow NH_2{\cdot}CHR'{\cdot}C(OH)R_2$$

(Bettzieche *et al.*, Z. physiol. Chem. 1924, **140**, 244 *et seq.* ; 1925, **146**, 227 ; **150**, 191).

Decarboxylation.—α-Amino-acids lose carbon dioxide when heated carefully (see, however, the section " Microchemical characterisation of amino-acids " for sublimation *in vacuo*), or with baryta, or (best) in a high boiling solvent (Johnson and Daschavsky, J. Biol. Chem. 1925, **62**, 725 ; Abderhalden and Gibelin, Z. physiol. Chem. 1926, **152**, 125), yielding the corresponding amines which are important pharmacologically, *e.g.* histamine, tyramine (Guggenheim, " Die Biogenen Amine," 1924, Springer, Berlin). These bases are also formed by decarboxylation of amino-acids by micro-organisms.

Micro-organisms decompose α-amino-acids in seven different ways, forming amines, alcohols, hydrocarbons, and saturated, unsaturated, and hydroxy-acids (Stephenson, " Bacterial Metabolism," 1930, p. 190, Longmans, Green and Co., London).

Influence of position of amino-group on mode of decomposition by heat.—The changes are analogous to those undergone by the corresponding hydroxy-acids.

α-Amino-acids or their esters lose water or alcohol (2 mols. from 2 mols. of acid or ester) and pass into *diketopiperazines*. With glycine ester the change takes place in water at room temperature. Such cyclic anhydrides, both *simple* and *mixed*, have been isolated after protein hydrolysis, and according to Abderhalden form an integral part of protein structures (for summary, *see* Klarmann, Chem. Rev. 1927, **4**, 51). Vickery and Osborne (Physiol. Rev. 1928, **8**, 393) conclude that Abderhalden has as yet failed to demonstrate conclusively that anhydride rings form any considerable fraction of the protein molecule, but the question of the presence of such rings is reopened by the observations of Shibata (Acta Phytochim. Japan, 1934, **8**, 173) that neutral diketopiperazines are not attacked by trypsin or pepsin, those having a carboxyl group are hydrolysed by trypsin, and those with a free amino-group are hydrolysed by pepsin (*see also* Tazawa, Acta Phytochim. Japan, 1935, **8**, 331).

In the case of β-amino-acids, 1 mol. of ammonia is eliminated from 1 mol. of the amino-acid ; thus β-alanine yields ammonia and acrylic acid when it melts with decomposition at 196°.

γ- and δ-Amino-acids and those with longer chains lose the elements of water and pass into cyclic acid amides (lactams), the reverse change being effected by hot, concentrated mineral acids. γ-Amino-butyric acid forms α-pyrrolidone, and δ-amino-valeric acid α-piperidone, when they melt with decomposition at 180° and 158° respectively.

Methylation yields betaines (Griess, Ber. 1875, **8**, 1406 ; Engeland, Ber. 1909, **42**, 2962 ; 1910, **43**, 2662 ; Engeland and Kutscher, Z. Biol. 1912, **59**, 415 ; Abderhalden and Schwaab, Z. physiol. Chem. 1925, **148**, 17 ; Zimmermann and Canzanelli, Z. physiol. Chem. 1933, **219**, 207 ; Dirr and Lang, Z. physiol. Chem. 1934, **225**, 79).

$$RCH(NH_2){\cdot}CO_2H \rightarrow RCH(\overset{+}{N}Me_3)\overset{-}{CO_2}$$

Attempts have been made to use betaines for the identification of amino-acids in proteins and in mixtures, but Vickery (quoted by Mitchell and Hamilton, " Biochemistry of the Amino-acids," 1929, 84, Chemical Catalog Co., New York) states that such separations are not easily effected.

Reduction with sodium and alcohol (Karrer *et al.*, Helv. Chim. Acta, 1921, **4**, 76 ; 1922, **5**, 469) converts α-amino-esters into amino-alcohols.

$$RCH(NH_2)CO_2Et \rightarrow RCH(NH_2)CH_2{\cdot}OH$$

Oxidation attacks initially the α-carbon atom, yielding keto-acids. Thus alanine ethyl ester is converted by permanganate into ethyl pyruvate (Goldschmidt and Beuschel, Annalen, 1926, **447**, 197), and amino-acids are transformed into keto-acids by kidney cells (in presence of arsenious acid to arrest further action) (Krebs, Z. physiol. Chem. 1933, **217**, 191 ; **218**, 157).

The usual products of the oxidation of an amino-acid are the corresponding aldehyde or acid, ammonia, and carbon dioxide :

$$RCH(NH_2)CO_2H \rightarrow RCHO + NH_3 + CO_2$$

and the following reagents (list not complete) bring about this change either catalytically with oxygen or by direct oxidation : permanganate (Sjollema and Dienske, Rec. trav. chim. 1933, **52**, 229) ; chromic acid ; oxygen and charcoal (Warburg and Negelein, Biochem. Z. 1921, **113**, 257 ; Ellinger and Landsberger, Z. physiol. Chem. 1922, **123**, 264 ; Wieland and Bergel, Annalen, 1924, **439**, 196 ; Gradwohl, Biochem. Z. 1930, **219**, 136 ; Bergel and Bolz, Z. physiol. Chem. 1933, **215**, 25) ; hydrogen peroxide (Dakin, J. Biol. Chem. 1908, **4**, 63 ; 1909, **5**, 409 ; Neuberg, Biochem. Z. 1909, **20**, 531) ; lead peroxide and sulphuric acid (Liebig, Annalen, 1849, **70**, 311) ; iron salts in light (Neuberg, Biochem. Z. 1908, **13**, 305) ; methyl glyoxal (Neuberg and Kobel, Biochem. Z. 1927, **188**, 198 ; Kisch, Biochem. Z. 1933, **257**, 334) ; silver oxide (Herbst and Clarke, J. Biol. Chem. 1934, **104**, 769) ; alloxan, isatin, quinones, dithioglycollic acid, dinitrobenzene, and palladium (Strecker, Annalen, 1862, **123**, 363 ; Hurtley and Wooton, J.C.S. 1911, **99**, 288 ; Traube, Ber. 1911, **44**, 3145 ; Bach, Biochem. Z. 1914, **58**, 205 ; Kisch, Biochem. Z. 1932, **244**, 440 ; Langenbeck, Ber. 1927, **60**, 930 ; 1928, **61**, 942 ; Wieland and Bergel, *l.c.*) ; sugars (Akabori, Ber. 1933, **66** [B], 143) ; sodium hypochlorite (Langheld, Ber. 1909, **42**, 392, 2360 ; Lieben and Bauminger, Biochem. Z. 1933, **261**, 387) ; chloramine-T (1 mol.)

(**Dakin** *et al.*, Proc. Roy. Soc. 1917, **89**, 232); **adrenaline and related amines (Edlbacher and Kraus**, Z. physiol. Chem. 1928, **178**, 239; Kisch, Biochem. Z. 1930, **220**, 370; Fermentforsch. 1932, **13**, 433; Barrenscheen and Danzer, Z. physiol. Chem. 1933, **220**, 57); **lead peroxide anode** (Takayama, Bull. Chem. Soc. Japan, 1933, **8**, 213).

a-Amino-acids are oxidised to nitriles by **chloramine-T** (2 mols.) (Dakin, Biochem. J. 1916, **10**, 319).

$$RCH(NH_2)CO_2H \rightarrow RCN + 4HCl + CO_2$$

Aminolysis.—The amino-group of *a*-amino-acids in aqueous solution is replaced by hydroxyl under the influence of charcoal in absence of oxygen (Wunderly, Z. physikal. Chem. 1924, **112**, 175; Helv. Chim. Acta, 1932, **15**, 721; 1933, **16**, 80, 1009; 1934, **17**, 523; Naturwiss. 1932, **20**, 873; Molinari, Helv. Chim. Acta, 1931, **14**, 671; Baur, Z. physikal. Chem. Bodenstein Festband, 1931, 162; Helv. Chim. Acta, 1933, **16**, 88; Baur and Wunderly, Biochem. Z. 1933, **262**, 300; Wieland and Bergel, Annalen, 1924, **439**, 196). Wieland, Drishaus, and Koschara (Annalen, 1934, **513**, 203) do not confirm this, but find that alanine, for example, gives acetaldehyde, ammonia, and carbon dioxide.

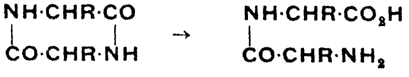
Synthesis of peptides.

$$NH_2{\cdot}CHR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO{\cdot}\ldots\ldots\ldots{\cdot}NH{\cdot}CHR''{\cdot}CO_2H$$

Papers dealing with the production of peptides from amino-acids form an immense volume of literature for which reference must be made to Fischer, "Untersuchungen über Aminosäuren, Polypeptide, und Proteine," 1899–1906, Springer Berlin, 1906; Vol. 2, 1907–1919, Springer, Berlin, 1923; Plimmer, "Chemical Constitution of the Proteins," Part 2, Longmans, Green and Co., 1913, pp. 27–43; Abderhalden and Fodor, Ber. 1916, **49**, 561; papers by Abderhalden and collaborators in Fermentforschung; and to many other sources. Special attention is directed to the use of benzylcarbonyl chloride by Bergmann (*see* acyl derivatives) in the synthesis of peptides.

Three general methods are employed:

1. The formation and partial hydrolysis of amino-acid anhydrides (diketopiperazines):



Hydrolysis of mixed **anhydrides** of **serine** and another amino-acid, *e.g.* **tyrosine**, proceeds in two ways depending on the reagent used. Alkaline hydrolysis gives tyrosyl-serine, acid hydrolysis seryl-tyrosine (Abderhalden and Bahn, Z. physiol. Chem. 1935, **234**, 181).

2. Acylation of an amino-acid or peptide (or ester) by an *a*-halogenated acid, and replacement of the halogen by ammonia:

$$\begin{gathered} BrCHR{\cdot}COCl + H_2N{\cdot}CHR'{\cdot}CO_2H \\ \longleftarrow \\ BrCHR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \\ \downarrow NH_3 \\ NH_2{\cdot}CHR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \end{gathered}$$

3. **Interaction of amino-acid chlorides** (or acylated **amino-acid chlorides**) with amino-acids or **peptides**, followed by removal of the acyl group if **present**:

$$\begin{gathered} NH_3Cl{\cdot}CHR{\cdot}COCl + NH_2{\cdot}CHR'{\cdot}CO_2H \\ \downarrow \\ NH_2{\cdot}CHR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \\ \uparrow \\ R''CO{\cdot}NH{\cdot}CHR{\cdot}COCl + NH_2{\cdot}CHR'{\cdot}CO_2H \end{gathered}$$

Compounds with sugars, glycerol, or fatty acids.—Series of derivatives have been prepared in which amino-acid radicals are condensed with **sugars** (esters of the carboxyl and hydroxyl groups, Bergmann and Zervas, Ber. 1932, **65** [B], 1201; Bergmann, Zervas, and Overhoff, Z. physiol. Chem. 1934, **224**, 52) (glucosides of the amino-group, v. Euler and Zeile, Annalen, 1931, **487**, 163; Maurer and Schiedt, Z. physiol. Chem. 1932, **206**, 125; **213**, 110; 1935, **231**, 1) (peptide-like substances from amino-sugars, Bertho and Maier, Annalen, 1932, **495**, 113); with glycerol (Abderhalden and Guggenheim, Z. physiol. Chem. 1910, **65**, 53; Abderhalden and Baumann, Z. physiol. Chem. 1911, **72**, 50; Wiezmann and Haskelberg, Compt. rend. 1929, **189**, 104); and with fatty acids (acyl derivatives) (Abderhalden and Funk, Z. physiol. Chem. 1910, **65**, 61).

OPTICAL PROPERTIES.

Molecular asymmetry.—The molecules of all *a*-amino-acids, except glycine, are asymmetric, and the naturally occurring members are all optically active. In a few cases also the molecule contains a second asymmetric carbon atom, so that four optically active forms are possible, *e.g. iso*leucine,

$$MeEt\overset{*}{C}H{\cdot}\overset{*}{C}H(NH_2)CO_2H,$$

and *β*-hydroxyglutamic acid,

$$CO_2H{\cdot}CH_2{\cdot}\overset{*}{C}H(OH)\overset{*}{C}H(NH_2)CO_2H$$

Probably only one of the active forms of an amino-acid exists in nature. With few exceptions the naturally occurring *a*-amino-acids belong to the *l*-series of Wohl and Freudenberg (Ber. 1923, **56** [B], 309). The sign and value of rotation are independent of the configuration at the *a*-carbon atom and are determined largely by the nature of the solvent, being a function of the degree of dissociation (*cf.* Levene, Bass, Rothen, and Steiger, J. Biol. Chem. 1929, **81**, 687; for summary and bibliography of optical rotations, *see* Mitchell and Hamilton, "Biochemistry of the Amino-acids," 1929, 64, Chemical Catalog Co., New York).

Whilst amino-acids obtained from proteins by acid hydrolysis are optically active, those obtained by alkaline hydrolysis, or by acid hydrolysis after alkaline treatment, are for the most part inactive. Since free amino-acids are not so readily racemised by alkali, this is explained (Dakin, J. Biol. Chem. 1912, **13**, 357; Dakin and Dudley, J. Biol. Chem. 1912, **25**, 263) by enolisation of the peptide linkages of the protein and racemisation at the *a*-carbon atom when the compound is hydrolysed or reverts to the keto-form on acidification. The terminal amino-acids with free carboxyl groups remain unracemised :

$$\begin{array}{c} CO_2H\cdot CHR\cdot NH\cdot CO{-}CHR\cdot NH_2 \\ \downarrow\uparrow \\ CO_2H\cdot CHR\cdot NH\cdot C(OH){=}CR\cdot NH_2 \end{array}$$

Racemisation may also be caused by heating with concentrated mineral acids, *e.g.* arginine by sulphuric acid (Kutscher, Z. physiol. Chem. 1901, **32**, 478 ; Reisser, Z. physiol. Chem. **1906**, **49**, 222).

Resolution of synthetic amino-acids is effected either chemically or enzymically :

1. By acylating (the formyl group is especially suitable) the amino-group, thereby producing a stronger acid ; resolving the salt of this acid with an optically active base ; and removing the acyl groups from the optical isomerides by hydrolysis (*e.g.* Fischer and Warburg, Ber. 1905, **38**, 3997).
2. By taking advantage of the fact that enzymes act on the naturally occurring forms of the amino-acids but not on their optical antipodes (*e.g.* Ehrlich, Biochem. Z. 1906, **1**, 8 ; 1914, **63**, 382 ; Riesser, Z. physiol. Chem. 1906, **49**, 232 ; Abderhalden, Sickel, and Ueda, Fermentforsch. 1923, **7**, 91).

Optical characteristics.—Keenan (J. Biol. Chem. 1924, **62**, 163 ; 1929, **83**, 137) has recorded the crystal habits, refractive indices, characters in parallel and converging polarised light, and diagnostic characters of thirteen important amino-acids.

Ultra-violet absorption spectra.—Amino-acids with an aromatic group, *e.g.* phenylalanine, tyrosine, tryptophane, absorb ultra-violet light selectively, whereas the aliphatic amino-acids show only general absorption. Cystine has slight selective absorption (Kober, J. Biol. Chem. 1915, **22**, 433 ; Ward, Biochem. J. 1923, **97**, 37 ; Marchlewski and Nowotnówna, Bull. Inter. Acad. Polonaise, 1925, **5–6**, A. 153 ; Abderhalden and Haas, Z. physiol. Chem. 1926, **160**, 256 ; Shibata and Asahina, Bull. Chem. Soc. Japan, 1927, **2**, 324 ; Ley and Arends, Ber. 1928, **61** [B], 212 ; Smith, Proc. Roy. Soc. 1929 [B], **104**, 198 ; Gróh and Hanák, Z. physiol. Chem. 1930, **190**, 169 ; Gutmann, Schwerin, and Stähler, Strahlentherap. 1931, **39**, 401 ; Anslow and Foster, J. Biol. Chem. 1932, **97**, 37).

ZWITTERION CONSTITUTION.

The amphoteric character of the amino-acids has long been recognised. Formerly it was considered that the dissociation constant involved in titrating in the acid range of p_H concerned the amino-group, whereas titration on the alkaline side of neutrality gave the acid dissociation constant. At the isoelectric point the amino-acid was believed to be practically undissociated. Adams (J. Amer. Chem. Soc. 1916, **38**, 1503) suggested that the reverse significance should be attached to these constants, and Bjerrum (Z. physikal. Chem. 1923, **104**, 147) regards the amino-acid in neutral solution as present almost entirely as "zwitterion," $^+NH_3\cdot CHR\cdot CO_2^-$. Addition of acid to the zwitterion suppresses ionisation of the carboxyl group, forming $^+NH_3\cdot CHR\cdot CO_2H$ ions, and similarly addition of alkali results in $NH_2\cdot CHR\cdot CO_2^-$ ions. Titration through the acid range of p_H therefore involves the carboxyl group, and through the alkaline range the amino-group. Bjerrum's views offer a rational explanation of the properties of amino-acids, *e.g.* their neutrality and high melting-points, their insolubility in alcohol and ether, their power of increasing the solubility of salts and of dissolving more readily in salt solutions than in water. Cohn (Ann. Rev. Biochem. 1935, **4**, 93) gives a comprehensive review of the physical properties of amino-acids, dimensions of constituent groups, electric moments, specific gravities, melting-points, solubilities, amphoteric properties, in the light of the newer knowledge of zwitterionic structure. Kuhn and Martin (Ber. 1934, **67** [B], 1526) discuss molecular structure as revealed by measurements of dielectric constants.

Much research has recently been published substantiating the zwitterionic nature of amino-acids in solution and in the solid state :—

1. *In solution* : Ley and Zschacke, Ber. 1924, **57** [B], 1700 ; Michaelis and Mizutani, Biochem. Z. 1924, **147**, 7 ; Ebert, Z. physikal. Chem. 1926, **121**, 385 ; Hedestrand, Z. physikal. Chem. 1928, **135**, 36; Harris, Proc. Roy. Soc. 1929 [B], **104**, 412 ; Biochem. J. 1930, **24**, 1080 ; Birch and Harris, Biochem. J. 1930, **24**, 564 ; Borsook and McFadyen, J. Gen. Physiol. 1930, **13**, 509 ; Emerson and Kirk, J. Biol. Chem. 1930, **87**, 597 ; Weber, Biochem. Z. 1930, **218**, 1 ; Kolthoff, Säure-Basen Indikatoren, 1932, 4th ed., p. 54, Berlin ; Ley and Arends, Z. physikal. Chem. 1932, **17**, 177 ; Miyamoto and Schmidt, Univ. Calif. Pub. Physiol. 1932, **8**, 1 ; Anslow *et al.*, J. Biol. Chem. 1933, **103**, 81 ; Edsall and Blanchard, J. Amer. Chem. Soc. 1933, **55**, 2337 ; Greenstein, J. Biol. Chem. 1933, **101**, 603 ; Wyman and McMeekin, J. Amer. Chem. Soc. 1933, **55**, 908, 915 ; Kirkwood, J. Chem. Physics, 1934, **2**, 351, 713 ; Neuberger, Proc. Roy. Soc. 1934 [B], **115**, 180 ; Richardson, Proc. Roy. Soc. 1934 [B], **115**, 121.
2. *In solid state* : Hengstenberg and Lenel, Z. Krist. 1931, **77**, 424 ; Bernal, Z. Krist. 1931, **78**, 363 ; Czarnetzky and Schmidt, J. Biol. Chem. 1932, **97**, 333.

ISOLATION, ESTIMATION, AND DETECTION.

Isolation.—Many processes for isolating individual amino-acids are described in the literature, but the following are general methods of group separation after protein hydrolysis.

1. Distillation under reduced pressure (Fischer, Ber. **1906**, **39**, 530) of the mixed ethyl esters separates the volatile esters of most monoamino-monocarboxylic acids and of the dibasic acids from the esters of the diacidic amino-acids (hexone bases) and a few others such as cystine and tyrosine, which form the non-volatile residue. For the preparation of the esters from the ester hydrochlorides, *see* Abderhalden, Z. physiol. Chem. 1922, **120**, 208 ; Levene, J. Biol.

Chem. 1909, **6**, 419 ; Uchida and Ai, J. Soc. Chem. Ind. Japan, 1933, **36**, 221.

2. Butyl alcohol extraction (Dakin, Biochem. J. 1918, **12**, 290 ; J. Biol. Chem. 1920, **44**, 499 ; Z. physiol. Chem. 1923, **130**, 161) removes (*a*) monoamino-monocarboxylic acids, and (*b*) proline and hydroxyproline from dibasic and diacidic amino-acids, and also separates (*a*) from (*b*).

3. The carbamate method (Buston and Schryver, Biochem. J. 1921, **15**, 636 ; Kingston and Schryver, Biochem. J. 1924, **18**, 1070) is especially useful for isolating the dicarboxylic acids.

4. Electrodialysis (Foster and Schmidt, J. Biol. Chem. 1923, **56**, 545 ; J. Amer. Chem. Soc. 1926, **48**, 1709) separates acidic, basic and neutral amino-acids.

5. Precipitation of hexone bases as phosphotungstates and silver salts (Kossel and Kutscher, Z. physiol. Chem. 1900, **31**, 165 ; Kossel and Patten, Z. physiol. Chem. 1903, **38**, 39 ; Vickery and Leavensworth, J. Biol. Chem. 1928, **76**, 707).

Mitchell and Hamilton (" Biochemistry of the Amino-acids," 1929, Chemical Catalog Co., New York, give a bibliography of these and other methods of separation, and Winterstein (" Handbuch der Pflanzenanalyse," 1933, **4**, 112–177) gives practical details for separating the amino-acids of protein hydrolysates and of plant extracts and also describes a number of examples of separating individual amino-acids from each other.

Estimation.—Many special methods have been devised for the estimation of individual amino-acids, but the following are generally applicable :

1. Colorimetric estimation by means of ninhydrin (triketohydrindene hydrate). *See* section on colour reactions below.

2. Titration with alkali in presence of formaldehyde to estimate amino-groups (Sørensen, Biochem. Z. 1907, **7**, 45 ; Northrop, J. Gen. Physiol. 1926, **9**, 767 ; references to section on condensation with aldehydes, p. 320).

3. Titration in alcohol with alcoholic potassium hydroxide using phenol- or thymolphthalein as indicator, to estimate amino-groups (Foreman, Biochem. J. 1920, **14**, 451 ; Willstätter and Waldschmidt-Leitz, Ber. 1921, **54**, 2988).

4. Titration in acetone with alcoholic hydrochloric acid, using naphthyl-red as indicator, to estimate carboxyl groups (Lindestrøm-Lang, Compt. rend. Trav. Lab. Carlsberg, 1927, **17**, No. 4).

5. Estimation of nitrogen evolved by interaction of nitrous acid with amino-groups (van Slyke) (*see* section on deamination by nitrous acid, p. 320).

Richardson (Proc. Roy. Soc. 1934 [B], **116**, 121) has discussed and compared methods 2–5.

Colour Reactions.—All α-amino-acids give a blue colour when heated in neutral solution with ninhydrin (triketohydrindene hydrate) (Ruhemann, J.C.S. 1910, **97**, 2025 ; Abderhalden and Schmidt, Z. physiol. Chem. 1911, **72**, 37 ; 1913, **85**, 143 ; Rettinger, J. Amer. Chem. Soc. 1917, **39**, 1059). For reaction with proline and hydroxyproline, *see* Grassmann and v. Arnim (Annalen, 1934, **509**, 288). The reaction is very sensitive, but is not specific, since it is also given by ammonia in sufficient concentration (Neuberg, Biochem. Z. 1913, **56**, 500 ; 1914, **67**, 56 ; Harding and Warneford, J. Biol. Chem. 1916, **25**, 319 ; Harding and MacLean, J. Biol. Chem. 1916, **25**, 337). Colorimetric estimations of amino-acids have been based on this reaction (Harding and MacLean, J. Biol. Chem. 1915, **20**, 217 ; 1916, **24**, 503 ; Riffart, Biochem. Z. 1922, **131**, 78).

Sodium β-naphthaquinone sulphonate gives a red colour with amino-acids and this has been used for their estimation in blood filtrates (Folin, J. Biol. Chem. 1922, **51**, 377).

Amino-acids give red colours with alloxan, the intensities of which vary with individual amino-acids (Lieben and Edel, Biochem. Z. 1932, **244**, 403).

A number of amino-acids give yellow to brownish-red precipitates with Nessler's reagent and may thus be distinguished from those which do not give the reaction (Sannié and Truhaut, Compt. rend. 1933, **196**, 65).

The individual amino-acids (*q.v.*) give colour reactions which depend on the presence of a specifically reactive group in their molecule, *e.g.* tyrosine, tryptophane, histidine, cysteine, arginine, canavanine (bibliography, Mitchell and Hamilton, " Biochemistry of the Amino-acids," 1929, 50, Chemical Catalog Co., New York).

α-Amino-acids do not give the biuret reaction, although their amides do so (Rising and Yang, J. Biol. Chem. 1933, **99**, 755).

Microchemical characterisation (Werner, Mikrochem. 1923, **1**, 33). The method depends on the fact that many amino-acids may be sublimed *in vacuo* yielding characteristic crystalline forms (*see* J. W. Brown, Trans. Roy. Soc. Canada, 1932 [iii], **26**, III, 173). Further definition of the sublimates is effected by a study of the precipitation by phosphotungstic acid and of the properties of the copper salts.

METHODS OF SYNTHESIS.

1. Ammonia, usually in the form of the concentrated solution but occasionally as the pure liquid, readily replaces the halogen atom of the α-halogenated fatty acids.

$$BrCHR{\cdot}CO_2H+2NH_3 \rightarrow NH_2{\cdot}CHR{\cdot}CO_2H+NH_4Br$$

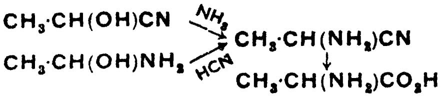
Experimental details of a preparation of this type are given in Organic Syntheses (1925, **4**, 3, 9) (the conversion of caproic acid into α-aminocaproic acid). A convenient modification of the earlier stage of this method was first devised by Fischer and Schmitz (Ber. 1906, **39**, 351), who obtained an almost quantitative yield of a bromo-alkylmalonic acid,

$$CRBr(CO_2H)_2,$$

by brominating the alkyl-malonic acid. Carbon dioxide was then eliminated by heat, and the resulting α-bromo-acid was converted into the amino-acid by ammonia.

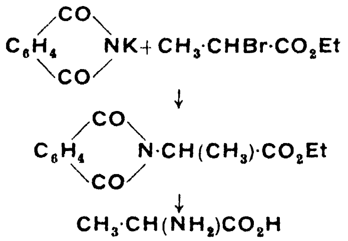
2. α-Amino-acids may often be easily obtained by the Strecker reaction (Annalen, 1850, **75**,

29), the interaction of ammonia with the cyanohydrins of the aldehydes (ketones), or of prussic acid with the aldehyde-ammonias. The resulting α-amino-nitriles yield amino-acids when hydrolysed.

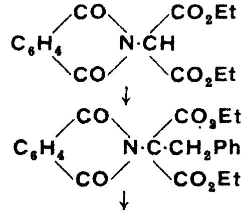


In practice the aldehyde is treated with a mixture of equivalent amounts of potassium cyanide and ammonium chloride (Zelinsky and Stadnikow, Ber. 1906, **39**, 1722). Recent improvements are given by Cocker and Lapworth (J.C.S. 1931, 1391) and by Anslow and King (J.C.S. 1929, 2463) and experimental procedure is detailed in Organic Syntheses (1925, **4**, 31, 47 ; 1929, **9**, 4 ; 1931, **11**, 4). The reaction may also be applied to substituted aldehydes ; thus, Fischer (Chem. Zentr. 1902 [i], 762) transformed glycollic aldehyde into serine.

3. Gabriel's phthalimide reaction may be applied to halogen-substituted esters, for example, ethyl α-bromopropionate yields alanine after complete hydrolysis by hot concentrated hydrochloric acid of its phthalimide derivative.

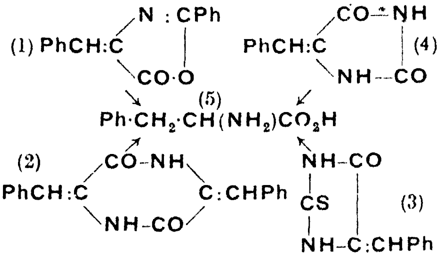

C_6H_4
CO
NK + $CH_3 \cdot CHBr \cdot CO_2Et$
CO
C_6H_4
CO
$N \cdot CH(CH_3) \cdot CO_2Et$
CO
$CH_3 \cdot CH(NH_2)CO_2H$

The following important extension of this method was made by Sørensen (Z. physiol. Chem. 1905, **44**, 448). Phthalimidomalonic ester is readily formed by the interaction of potassium phthalimide and bromomalonic ester (for details *see* Organic Syntheses, 1927, **7**, 34, 78). The remaining hydrogen atom of the methylene group may then be replaced successively by sodium and by alkyl in the usual way. Using benzyl chloride, for example, benzylphthalimidomalonic ester is formed and is converted by suitable hydrolytic treatment into phenylalanine.



Since any substituted alkyl group may be introduced into the malonic ester residue, this forms a convenient method of preparing any α-amino-acid, and it has frequently been used for the synthesis of members of classes 1, 2, and 3 of the amino-acids (*see* above) and of hydroxy-amino-acids.

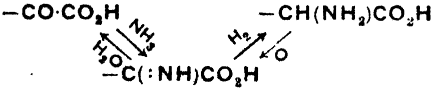
4. α-Amino-acids may readily be obtained by Erlenmeyer's method (Annalen, 1893, **275**, 1 ; 1899, **307**, 70, 138 ; 1901, **316**, 145), which has been applied chiefly, but not entirely, to the synthesis of amino-acids containing cyclic structures (*see* Lamb and Robson, Biochem. J. 1931, **25**, 1231, for bibliography and modifications). The azlactone (1) prepared by condensing benzaldehyde with hippuric acid in the presence of sodium acetate and hot acetic anhydride, or 2 : 5-dibenzylidenepiperazine (2) similarly prepared from benzaldehyde and 2 : 5-diketopiperazine (Sasaki, Ber. 1921, **54** [B], 163, 2056) yield *dl*-phenylalanine (5) on reduction and hydrolysis ; or benzylidene thiohydantoin (3) may be transformed directly into phenylalanine by acid reduction (Johnson and O'Brien, J. Biol. Chem. 1912, **12**, 205). The technique of a third alternative, condensation of a suitable aldehyde with hydantoin followed by hydrolytic reduction of the product (4) to the amino-acid (Wheeler and Hoffmann, Amer. Chem. J. 1911, **45**, 368), has recently been improved by Boyd and Robson (Biochem. J. 1935, **29**, 542, 546, 555, 2256).



5. Reduction of the oximes or hydrazones of ketonic acids is a general method for preparing amino-acids (α, β, γ, etc., according to the position of the carbonyl group) (Tafel, Ber. 1886, **19**, 2414 ; Knoop and Hoessli, Ber. 1906, **39**, 1477 ; Fischer and Groh, Annalen, 1911, **383**, 363 ; Anziegin and Gulewitsch, Z. physiol. Chem. 1926, **158**, 32 ; Harington and Randall, Biochem. J. 1931, **25**, 1917).

$$-CO \cdot CO_2H \rightarrow -C(:NOH)CO_2H \rightarrow -CH(NH_2)CO_2H$$

6. α-Amino-acids are produced by the reduction of an α-keto-acid in presence of ammonia, either catalytically (2 mols. of ammonia give the best yield), or with sodium amalgam, ferrous iron, or physiological reducers such as cysteine (de Jong, Rec. trav. chim. 1900, **19**, 259 ; Erlenmeyer and Kunlin, Ber. 1902, **35**, 2438 ; Annalen, 1899, **307**, 146 ; Knoop and Oesterlin, Z. physiol. Chem. 1925, **148**, 294 ; 1927, **170**, 186). The change probably occurs through the intermediate ketimino-acid which is unstable in water (Goldschmidt and Beuschel, Annalen, 1926, **447**, 197). The reaction is reversible, since oxidation of the amino-acid by permanganate yields the keto-acid and ammonia.



Amino-acids in nutrition and metabolism.—*See* Mitchell and Hamilton, "Biochemistry of the Amino-acids," 1929, Chemical Catalog Co., New York; McCollum and Simmonds, "The Newer Knowledge of Nutrition," 1929, Macmillan; Ann. Rev. Biochem. 1932, **1**, 299; 1933, **2**, 165; 1934, **8**, 193; 1935, **4**, 225. J. M. G.

d-**AMINOBUTYRIC ACID** *v.* Amino Acids.

a-**AMINOCAPROIC ACID** *v.* Leucine.

p-**AMINOCARVACROL.** A photographic developer, resembling both metol and *p*-aminophenol in this property; its solution keeps better than that of the latter. Obtained by reducing an ammoniacal solution of *p*-nitroso carvacrol by hydrogen sulphide when *p*-amino carvacrol separates in colourless leaves (Brit. J. Phot. 1919, **56**, 534).

β-**AMINOETHYL ALCOHOL** *v.* Choline.

4-*β*-**AMINOETHYLGLYOXALINE** *v.* Ergot.

AMINOFORM, Cystamine, Cystogen, Formamine, Formin, Hexamine, Metramine, Uritone, Urotropin, and Vesalvine, are trade names for hexamethylenetetramine, $(CH_2)_6N_4$. Crystals subliming with partial decomposition at about 263°. Urinary antiseptic.

AMINOPHYLLIN. Euphyllin. Trade name for a compound of theophylline,

$$C_5H_2(CH_3)_2O_2N_4{\cdot}H_2O,$$

and ethylene diamine, $C_2H_4{\cdot}[NH_2]_2$. Diuretic.

AMMINES. Complex metal-ammonium compounds, *v.* Coordination Compounds.

AMMODENDRINE,

$$C_{12}H_{22}N_2O_2,H_2O,$$

m.p. 73°–74°, optically inactive, is a monacid secondary base present in *Ammodendron Conollyi* Bge (0·7%) along with *d*-sparteine (1·1%) (Orechoff and Proskurnina, Ber. 1935, **68** [B], 1807). G. B.

AMMONAL. A blasting explosive, also used for military purposes. As introduced by Roth of Vienna, in the year 1900, it consisted of ammonium nitrate (A/N), aluminium powder, and charcoal. Later a proportion of the A/N was replaced by trinitrotoluene (T.N.T.), giving greater explosive power and ease of detonation. The percentage compositions of typical examples of Roth's ammonal were as follows:

A/N	80	90	46	32
T.N.T. . . .	—	—	30	50
Aluminium . .	18	4	22	16
Charcoal . . .	2	6	2	2

For military purposes the following percentage compositions have been used, chiefly for land mines and for grenades:

	Austrian.	German.	French.	British.
A/N . . .	45	54	65	65
T.N.T. . .	30	30	15	15
Aluminium .	23	16	10	17
Charcoal . .	2	—	10	3

The explosive properties of ammonal are similar to those of amatol (*q.v.*), the effect of the aluminium being to increase the temperature, and therefore the power, of the explosion by conversion of the metal into its oxide at the moment of detonation. It is stated that the explosive power of A/N, as determined by lead-block test (*see* Explosives), is increased 2½ times by the addition of 20% of aluminium powder. The course of the explosive reaction may be expressed by the following equation:

$$4NH_4NO_3+2Al+C =4N_2+8H_2O+Al_2O_3+CO$$

The formation of carbon monoxide as one of the products of explosion precludes the use of ammonal for underground mining unless a considerable excess of A/N is present in the mixture. The following percentage compositions, however, were formerly on the Permitted List for use in coal mines:

	Ammonal B.	Ripping Ammonal.	St. Helen's Powder.
A/N . .	94·5	86	93·5
T.N.T. . .	—	—	4
Aluminium	3	8	2·5
Charcoal .	2·5	2·5	—
Potassium dichromate	—	3·5	—

Military ammonal is comparatively insensitive and cannot be exploded by the impact of a bullet or by the application of a flame. Its use in the field, however, is limited by the fact that it is difficult to ensure its complete detonation if compressed to a density greater than 1·2, whereas an explosive of this type so lightly compressed would be liable to "set-back" in a high-velocity shell when discharged from the gun. It has been used in Austria, however, for filling trench mortar bombs.

On account of the hygroscopicity and corrosive character of A/N, all varieties of ammonal must be prepared, stored, and used under suitable precautions. In the mixtures containing T.N.T. this disadvantage may be overcome to a certain extent by coating the particles of A/N with molten T.N.T. before adding the other ingredients.

The aluminium powder for use in ammonal may be of the flake form, but the granular variety is more resistant to oxidation in storage and functions quite satisfactorily.

H. S.

AMMONIA.

Historical.—Certain compounds of ammonia, in particular "sal ammoniac" or ammonium chloride, were known to the ancients, but the existence of free ammonia was not clearly recognised until 1774, when Priestley prepared gaseous ammonia by distilling sal ammoniac with quicklime and collecting the gas over mercury. Priestley called it "alkaline air."

C. L. Berthollet in 1785 established its composition as NH_3 by decomposing it with the electric spark. More exact data were later obtained by Austin, Davy, Henry and A. B. Berthollet.

The introduction of coal distillation for gas-making towards the middle of the nineteenth century gave to ammonia for the first time a definite technical importance, although it, like tar, was at first treated as a troublesome by-product. This importance grew as the work of Liebig and that of Lawes and Gilbert led to the general recognition of the value of artificial fertilisers (in particular nitrogenous fertilisers), and as a result the production of ammonium sulphate from gasworks and by-product coke ovens became an industry of importance.

Other industrial applications of ammonia have followed—the ammonia-soda process, refrigeration, dyes, nitric acid and nitrates, explosives, etc. In the year 1934–35 the world's production of ammonia was nearly two million metric tons, of which by far the greater proportion was used for agricultural purposes.

In recent years, since 1913, the synthetic ammonia industry, making ammonia direct from hydrogen and atmospheric nitrogen, has grown enormously and has taken prior place as the supplier of the world's demand for ammonia and, indeed, for fixed nitrogen.

Occurrence.—Ammonia (or its salts) is found in small quantities in the air, in water and in the soil, in the animal body and in plants. One of the earliest sources of ammonia was decaying urine. Its natural occurrence is due in the main to the decomposition of nitrogenous organic matter and is of the utmost importance to agriculture ; the growth of plants depends largely on the ammonia thus present in the soil and on the nitrates formed by its oxidation. Concentrations varying from 0·4 mg./litre up to 5 mg. have been found in rain. In river and canal water amounts between 0·02 and 5 mg./litre have been variously reported, in sea water 0·10 to 1 mg./litre. Its presence in river water is often regarded as an indication of pollution by decaying organic matter. Certain varieties of peat, clays, marls, etc., have a high absorptive capacity for ammonia and the local concentration in such materials is high.

Ammonium carbonate is found in high concentration in certain concentrated decomposition products, as in the guano deposits of South America. Ammonium salts are also found in certain mineral deposits such as Stassfurt carnallite.

None of these natural sources of ammonia are of much technical significance. The technical sources are the nitrogen in air and the accumulated nitrogen in coal, lignite, etc., which had its origin in atmospheric nitrogen.

Formation.—Ammonia is formed in small but definite quantities when a mixture of nitrogen and hydrogen is exposed to an electric discharge (Morren, Geitz, and Perrot, Compt. rend. 1859, **48**, 342 ; 1859, **49**, 204). Findlay used a brush discharge (Z. Elektrochem. 1906, **12**, 129), while both Thénard (Compt. rend. 1873, **76**, 983) and Donkin (Proc. Roy. Soc. 1873, **21**, 281) observed the presence of ammonia using a silent discharge. Increase in pressure gives an increased yield of ammonia (Perman, Proc. Roy. Soc. 1905, **76A**, 167 ; 1904, **74A**, 110). Appreciable quantities of ammonium chloride are formed on passing sparks through a mixture of nitrogen, hydrogen, and hydrogen chloride (Deville, Compt. rend. 1865, **60**, 317) ; nitrogen and hydrogen can, in fact, be made to combine completely if the ammonia is continuously removed by an acid.

Nitrogen and hydrogen can also be combined to form ammonia by heating in the presence of catalysts. Using such catalysts as iron, osmium, uranium, etc., ammonia is formed in small quantities at temperatures of 450°–600°C. ; the conversion to ammonia is increased considerably under pressure. A fuller discussion of the direct synthesis of ammonia will be found below.

The equilibrium $N_2+3H_2 \rightleftharpoons 2NH_3$ may be set up at ordinary temperatures in the presence of platinum black or colloidal gold or platinum, when a mixture of nitrogen and hydrogen is passed through water rendered acid at 90°C. and containing these elements.

Ammonia is formed by the reduction of oxides of nitrogen or of nitrates, *e.g.* from a mixture of hydrogen and oxides of nitrogen on passing through heated platinum sponge, platinised asbestos or platinum black ; from nitric acid in contact with moist iron or tin filings, or an aqueous solution of H_2S ; from acidified solutions of nitrates by the action of zinc or iron.

Nitrogen phosphide, sulphide, iodide, and chloride yield ammonia on treatment with water. Certain cyanogen compounds, such as cyanates, form ammonia in the presence of moisture. Cyanides form ammonia on treatment with superheated steam ; calcium cyanamide, $CaCN_2$, which is made from atmospheric nitrogen according to the now well-known process of Frank and Caro, yields ammonia on treatment in this way.

Certain nitrides, such as those of silicon, magnesium, aluminium, react with water or steam to form ammonia. In the Serpek process aluminium nitride made by heating bauxite with carbon in an atmosphere of nitrogen is decomposed by boiling with an alkaline solution : potassium aluminate is formed, and can be used to decompose more nitride (B.P. 15997, 1909).

Ammonia is also formed from nitrogenous organic compounds. The earliest sources of ammonia were probably urine and camel's dung. Normal urine contains 20–35 g./litre of urea, and during putrefaction the urea is converted into ammonium carbonate. The ammonia in sewage is, however, usually too dilute for recovery.

When animal substances such as bones, horn, leather, hair, etc., are carbonised, animal charcoal remains, while ammonia and a tar rich in pyridine derivatives (known as "Dippel's oil") pass over. The old term for ammonia, "spirits of hartshorn," refers to the old practice of carbonising the hoofs and horns of stags, etc.

Similarly, in the distillation of coal (also lignite and peat) in coke ovens and gasworks, ammonia is produced as a by-product (*see below under* Technical Production).

For laboratory purposes the gas is usually obtained direct from cylinders of liquid ammonia (*see below under* Technical Forms of Ammonia), or by warming the concentrated solution or by heating a mixture of ammonium chloride or sulphate with quicklime or slaked lime. The gas is dried by passage through quicklime, since it reacts with the usual drying agents such as calcium chloride, concentrated sulphuric acid, or phosphorus pentoxide. Stas, in his work on atomic weights, used purified ammonium chloride (Bull. Acad. roy. Belg. 1860 [ii], **10**, 8); Burrell and Robertson (J. Amer. Chem. Soc. 1915, **37**, 2842) obtained very pure ammonia by distilling aqueous ammonia one or more times and then drying the gas over fused alkali hydroxide. A large number of more recent workers (*e.g.* McKelvey and Taylor, "Composition, Purification, and Certain Constants of Ammonia," Washington, 1923) have obtained the gas from a cylinder of the liquid and fractionally distilled it a number of times.

Physical Properties.—Ammonia is a colourless gas, with a pungent and characteristic odour. Animals die if submerged in the gas, which attacks the mucous membrane. Its density is 0·5967 (air = 1) or 0·5395 (O_2 = 1), or 0·7708 g. per litre at 0° and 760 mm. Ammonia readily liquefies on compression, the critical temperature being 132·4°C., the critical pressure 112 atmospheres, and the critical density 0·2364 g./c.c. According to Shilling, the specific heat of ammonia gas at constant pressure, C_p, is as follows :

Temperature °C.	C_p g.-cals./g. °C.	Ratio of specific heats.
0	0·510	1·315
14	0·514	1·309
100	0·537	1·284
200	0·567	1·262
300	0·597	1·244
400	0·629	1·228
500	0·664	1·214

According to Osborne, Simpson, Sligh, and Cragoe (U.S. Bur. Standards Sci. Paper, 1925, **20**, 65), C_p in joules/g. °C. is given by the following formula in the range −15° to +150°C. and 0·5 to 20 kg./cm.^{2} :

$$C_p = 1{\cdot}1255 + 0{\cdot}00238T + \frac{76{\cdot}8}{T} + \frac{5{\cdot}45p10^8}{T^4} + \frac{p(6{\cdot}5+3{\cdot}8p)10^{27}}{T^{12}} + \frac{2{\cdot}37p^6 10^{42}}{T^{20}},$$

T being the absolute temperature and p the pressure in metres of mercury at 0°C. (1 cal.$_{20}$ = 4·183 joule).

Ammonia is very soluble in water, as also in alcohol, ether, and many other solvents. The solubility in water at 1 atmosphere pressure is as follows, according to Roscoe and Dittmar ; determinations by Sims are also given for comparison :

Temp. °C.	c.c. NH_3 dissolved in 1 g. water.	g. NH_3 dissolved in 1 g. water. (Sims).	Strength of solution in equilibrium at 1 atm. total pressure. % NH_3 by weight.
0	1,148	0·875 (0·899)	46·7
10	891	0·679 (0·684)	40·4
20	690	0·526 (0·518)	34·5
30	529	0·403 (0·408)	28·7
40	403	0·307 (0·338)	23·5
50	300	0·229 (0·284)	18·6

In the act of solution much heat is evolved, according to Thomsen 8,430 g.-cals. per g. mol. NH_3, and according to Wrewsky and Sawaritzky 8,336 g.-cals. at 20°C. (495 and 489 g.-cals./g. respectively). This assumes dilution with a relatively large quantity of water ; the heat evolution in producing, by the solution of NH_3 gas in a finite amount of water, solutions of varying strength is shown below (derived from data by Mollier) :

Concentration of final solution % NH_3 by weight.	Heat of solution. g.-cals./ g. NH_3.	g.-cals./ g. mol. NH_3.
10	477	8123
20	463·5	7893
30	448·5	7638
40	431	7340
50	411·5	7008

The total vapour pressures of solutions of ammonia in water are given in Fig. 1 for low temperatures (Postma, Rec. trav. chim. 1920,

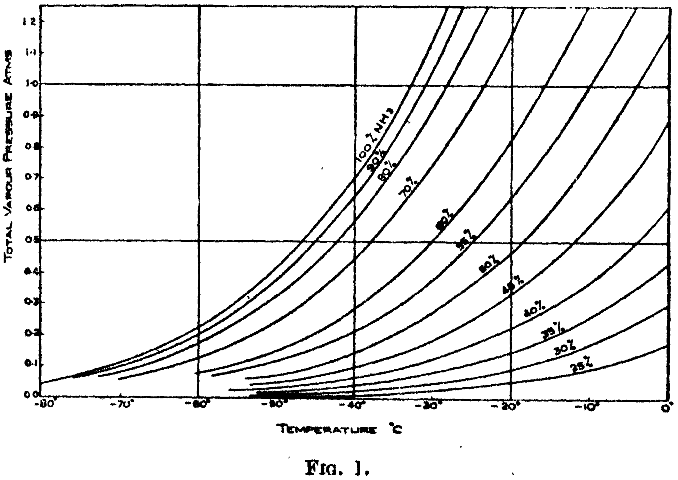


Fig. 1.

39, 515), and in Fig. 2 for more elevated temperatures (Perman, J. Chem. Soc. 1903, **83**, 1169 ; Mollier, Forsch. Ver. deut. Ing. 1909).

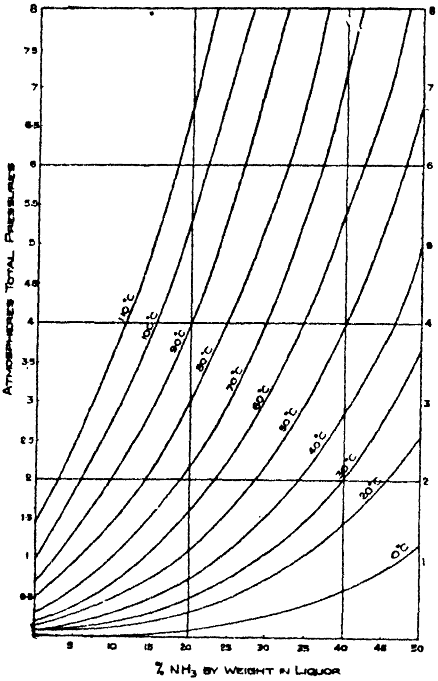


Fig. 2.

The table on p. 330 gives the specific gravity of aqueous solutions, according to the data of Lunge and Wiernik.

The specific heat of ammonia solutions is approximately the same as that of water. At 20·6°C. the specific heat of a 32·3% solution is 1·0128, and of a 15·07% solution 0·9946 (Wrewsky and Kaigorodoff).

Liquid ammonia is a colourless, mobile liquid, the density of which (water at 4°C.=1) is 0·6382 at 0°C. and 0·6901 at −40°C. (Holst). According to Timmermanns, the following formula covers the variation of density with temperature :

$$D_t = 0{\cdot}63860 - 134{\cdot}0t10^{-5} - 1365t^2 10^{-8}$$

The boiling-point under atmospheric pressure is −33·41°±0·1° (Bergstrom). The latent heat of vaporisation varies as follows (Osborne and van Dusen) :

Temp. °C.	Latent heat of vaporisation g.-cals./g. NH_3.
−40	331·7
−20	317·6
0	301·8
+20	283·8
+40	263·1

The vapour pressure of liquid NH_3 at various temperatures can be read from Figs. 1 and 3, taking the lines corresponding to 100% NH_3.

The specific heat of liquid NH_3 (C_p) varies as follows (Osborne and van Dusen) :

Temp. °C.	Specific heat g.-cals./g. °C.
−40	1·062
−20	1·078
0	1·099
+20	1·126
+40	1·162

At −77° to −78° (−77·73°±0·03°, according to Elliott) liquid ammonia freezes to a white crystalline solid of density 0·80 to 0·81. The ammonia vapour pressure at the melting-point is about 45 mm. Hg. The heat of fusion is 81–84 g.-cals. per g. at −81·5°C. (Eucken, Karwat, Donath). The specific heat of the solid is 0·50 g.-cals./g. °C. over the range −188°C. to −103°C. (Dewar), or 0·5095 at −138·6°C. (Clusius, Miller, and Vaughen).

The following values have been obtained for the heat of formation at ordinary temperature by burning ammonia at constant pressure :

11,890 g.-cals. per g. mol.—Thomsen.
12,200 g.-cals. per g. mol.—Berthelot and Matignon.

By direct decomposition in a calorimeter, using a catalyst, Haber and his co-workers (Z. Elektrochem. 1915, **21**, 191, 206) obtained the following values :

T °C.	0	466	503	554	659
Q .	10,950	12,670	12,700	12,900	13,150

Omitting the third value, which is discordant :

$$Q = 9{,}575 + 5{\cdot}535T - 0{\cdot}001822T^2$$

Chemical Properties.—Ammonia gas is only feebly combustible in air, the heat of combustion being insufficient to maintain a flame, but it burns vigorously in oxygen. The products of combustion are nitrogen, water, a small proportion of ammonium nitrate, and a trace of NO_2.

Oxidation proceeds at lower temperatures in the presence of catalysts, such as copper, iron, nickel and, in particular platinum, producing oxides of nitrogen. The Ostwald process for the manufacture of nitric acid from ammonia is based on this reaction (*see* Nitrogen, Nitric Acid). Gaseous ammonia is oxidised to steam and nitrogen by many oxides, *e.g.* copper oxide. Oxides of nitrogen when sparked or heated with ammonia also give steam and nitrogen. Under certain conditions a mixture of air and ammonia gas may be exploded by an electric spark (Schlumberger and Piotrowski, J. Gasbeleucht. 1914, **57**, 941).

Ammonia is decomposed into its elements by heating, the rate of decomposition being greatly affected by the nature of the surfaces with which the gases come in contact. Glass is very inactive, porcelain and pumice have a distinct accelerating effect, while metals such as iron, nickel, zinc, osmium, uranium, etc., have a very strong accelerating effect. The catalysts which are used for the direct synthesis of ammonia (and which are described below) are, of course, similarly effective in promoting the reverse reaction. The varying catalytic effect of

Specific Gravity of Aqueous Solutions of Ammonia at 15°C. (Lunge and Wiernik)

Sp.gr.	NH_3 %.	1 litre contains NH_3 in g.	Correction of sp.gr. for ±1°C.	Sp.gr.	NH_3 %.	1 litre contains NH_3 in g.	Correction of sp.gr. for ±1°C.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

different surfaces and the fact that the ammonia equilibrium was not properly understood before the present century account for much of the discrepancy between statements as to the extent of ammonia decomposition at different temperatures. Ramsay and Young (Trans. Chem. Soc. 1884, **45**, 88) noted the catalytic effect of iron and found that even when dry ammonia is passed slowly through a red-hot tube a trace of ammonia still remains undecomposed. The reaction was also studied by Perman (Proc. Roy. Soc. 1905, **76A**, 167: 1904, **74**, 110), and equilibrium conditions for the reversible reactions established by Haber and Van Oordt and other workers (*see below under* Technical Production). In general, it may be said that under atmospheric pressure decomposition sets in at about 450°-500°C., or with dry ammonia at about 600°C. In the presence of catalysts decomposition sets in as low as 300°C. and is nearly complete at 500°-600°C. ; even at 1,000°C., however, a small but definite trace of ammonia remains.

Incandescent wires of various metals are particularly effective in promoting the decomposition of ammonia ; the kinetics of the reaction under these conditions have been studied by Hinshelwood ("The Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, 1926).

Ammonia is completely decomposed by ultraviolet light (Coehn and Prigent, Z. Elektrochem. 1914, **20**, 275).

The ease with which ammonia can be decomposed with the aid of catalysts has led to the development of "cracked ammonia." Since liquid ammonia is more economical to transport than compressed hydrogen, it is used in combination with a cracking apparatus to replace hydrogen for metallurgical purposes, etc. (*see* Hydrogen).

A number of the elements when heated in ammonia gas yield the corresponding nitride ; boron, magnesium and titanium are especially active in this respect. With chlorine and bromine, free nitrogen and ammonium chloride or bromide are formed. With phosphorus vapour at red heat nitrogen and phosphine PH_3 are formed. Sulphur vapour gives nitrogen and ammonium sulphide ; carbon at red heat gives ammonium cyanide. The alkali metals give rise to amides, *e.g.* on passing dry ammonia over sodium heated to 300°-400°C. a white solid, sodamide NH_2Na, is formed. The amides of the alkali metals are also formed on warming a solution of the metal in liquid ammonia, or by double decomposition in liquid ammonia.

Many salts combine with ammonia to form stable compounds at the ordinary temperature, the ammonia playing a similar part to water of crystallisation, it is evolved on heating, and liquid ammonia was first obtained by Faraday in 1823 by warming $2AgCl,3NH_3$ in a sealed tube.

The solution of ammonia gas in water (ammonia liquor) is strongly alkaline and reacts with acids to form *ammonium* salts. It is frequently supposed, therefore, that the solution contains ammonium hydroxide, NH_4OH, analogous to $NaOH$ and KOH. The evidence for this is by no means conclusive. The work of Rupert (J. Amer. Chem. Soc. 1910, **32**, 748) and of Smits and Postma (Kon. Akad. Amst. Proc. 1909, **186** ; Rec. trav. chim. 1920, **39**, 515) has shown that two definite hydrates exist, the freezing-point curves of mixtures of ammonia and water showing three well-defined minima at −100·3°C., −86° to −87°C., and −92·5° to −94°C., corresponding to the eutectic mixtures $NH_3{\cdot}H_2O$+ice, $2NH_3{\cdot}H_2O+NH_3{\cdot}H_2O$, and $NH_3+2NH_3{\cdot}H_2O$ respectively. The presence of the ion NH_4 in solutions in low concentrations is demonstrated by electrochemical evidence, while Moore's experiments on the distribution ratios of ammonia between water and chloroform suggest the existence of comparable proportions of hydrate to hydroxide in solution (J.C.S. 1907, **91**, 1373 ; 1912, **101**, 1667).

The aqueous solution of ammonia dissolves many metallic oxides and hydroxides such as $Ag_2O,Cu(OH)_2$, etc., as well as many salts which are insoluble in water, such as silver chloride, silver phosphate and cuprous chloride. The solution of cupric hydroxide in ammonia is of considerable technical importance as a solvent for cellulose in, for example, the rayon industry.

Ammonium salts are anhydrous. They are sublimed, with dissociation, in the vapour phase and recombine on condensation. The more important technical salts are discussed below.

Liquid (anhydrous) ammonia is one of the most comprehensive solvents known. It dissolves the alkali metals (solubility of potassium 48·75 g./100 g. NH_3 at 0°C., of sodium 23·2 g./100 g. NH_3 at 0°C.—Ruff and Geisel, Ber. 1906, **39**, 838), non-metals such as sulphur, phosphorus and iodine, many halides and sulphides of the non-metals, and also many typical aqueous electrolytes. In concentrated solutions the ammonia vapour pressure is greatly reduced and may even lie well below 1 atm. Many organic compounds such as amides, nitro-compounds, alkyl ammonium bases, etc., also dissolve in liquid ammonia.

The ions present in such solutions react and frequently give quite unusual precipitates. Thus dissolved metals react to give alloys, *e.g.* sodium and lead give a precipitate of Na_2Pb_5, sodium and tellurium give Na_2Te and Na_2Te_2. Amides and nitrides are formed on interaction of, for example, potassamide with other salts in liquid ammonia solution, thus, $3HgI_2+6KNH_2=Hg_3N_2+6KI+4NH_3$. Magnesium dissolves in a liquid ammonia solution of ammonium chloride to give magnesium chloride, hydrogen and free ammonia. Acid amides dissolved in ammonia behave like carboxylic acids dissolved in water. A typical reaction is :

$$Mg+CH_3{\cdot}CONH_2=CH_3{\cdot}CONMg+H_2$$

Detection and Estimation.—The presence of moderate quantities of ammonia in a solution or in the air can be detected by smell, by the brown colour imparted to yellow turmeric paper or by an alkaline reaction to indicators. The indicators preferably used are methyl orange or methyl red, or others of the type sensitive to weak alkalis.

Traces of ammonia in solution as, for example, in water contaminated with organic matter, are detected by the use of Nessler's reagent, with which it gives a brown coloration; the depth of this coloration is often used for the quantitative estimation. Nessler's reagent is potassium mercuric iodide, K_2HgI_4, in excess of $NaOH$ or KOH. The brown colour obtained with ammonia is destroyed by acids and can thus be distinguished from that due to sulphides which is not destroyed.

Free ammonia present in a solution is normally estimated by titration with standard acid, using methyl orange or methyl red. It can be estimated gravimetrically by precipitation with chloroplatinic acid, weighing either as $(NH_4)_2PtCl_6$ or igniting and weighing as Pt.

TECHNICAL PRODUCTION.

General.—The modern processes of technical importance for the production of ammonia are (I) the direct synthetic process from hydrogen and atmospheric nitrogen and (II) the destructive distillation of nitrogenous organic matter, chiefly coal or lignite. Of these the synthetic process now predominates. Ammonia has in the past been recovered from urine, sewage, and animal excreta, from guano, from vinasse, etc., but these methods are now of minor importance or historical interest only.

The development of ammonia production in recent years by the synthetic process and as a by-product in coal distillation is seen clearly from the following statistics :

Fertiliser year.	Output (metric tons nitrogen).		
	Synthetic ammonia.	By-product ammonia.	Total world nitrogen.
1900	—	100,000	320,000
1910	—	210,000	570,000
1920	190,000	287,000	1,000,000
1925	345,300	324,900	1,152,000
1929/30	999,900	475,840	2,203,540
1930/31	852,822	390,534	1,694,288
1931/32	948,988	331,625	1,585,217
1932/33	1,140,325	297,279	1,676,859
1933/34	1,157,412	355,309	1,792,266
1934/35	1,264,184	360,334	2,041,366

The statistics from 1925 onwards are derived from the annual reports of the British Sulphate of Ammonia Federation. Those for 1900–1920 are approximate, and are taken from Waeser's "Atmospheric Nitrogen Industry," J. & A.

Churchill, 1926. Of the total nitrogen produced about 90% is consumed in agriculture, and of this over 45% is as ammonium sulphate.

The following figures for the production of ammonia in England and Wales (also as metric tons of nitrogen) are derived from the annual reports of the Chief Alkali Inspector :

	From gasworks.	From other works (incl. coke ovens, iron-works, producer gas, synthetic works, etc.).	Total.
1923	30,326	39,242	69,568
1930	30,176	120,252	150,428
1931	27,637	98,330	125,967
1932	20,743	132,923	153,666
1933	18,983	118,246	137,229
1934	21,698	97,290	118,988

The decline in the production from gasworks and the large increase since 1923 in the total for "other works" are due in the main to the operations of the Billingham Synthetic Ammonia plant, which started up in 1923.

I. The Direct Synthesis of Ammonia.

The direct synthesis of ammonia from its elements was at one time considered impossible. It was known that ammonia could be decomposed by heating or by the passage of electric sparks, but the question as to whether the reaction could be reversed was hotly contested for some years. Various investigators such as Ramsay and Young (J. Chem. Soc. 1884, **45**, 88), Perman (Proc. Roy. Soc. 1904, **74**, 110 ; 1905, **76A**, 16), and Ostwald demonstrated, however, that when ammonia is decomposed the reaction does not go to completion and a trace of ammonia is always left behind. The work of Haber, Nernst, and their co-workers in Germany showed conclusively that the reaction was reversible and led to a more complete understanding of the ammonia equilibrium, thus effectively laying the foundations of the synthetic ammonia industry.

In the years 1904–1908, Haber, Van Oordt, Le Rossignol, Nernst, Jellinek and Jost established equilibrium data for the system NH_3–N_2–H_2 over a range of temperatures and pressures. Haber and his co-workers also investigated a number of catalysts for the reaction. This work will be described in more detail below. In 1908 the Badische Anilin und Soda Fabrik (now part of the I.G.) undertook the financing of Haber's further work, and an increasing number of patents appear from that year. Haber's first patents were for the use of osmium and uranium as catalysts (G.P. 223408 and 229126), next appeared his patent proposing recirculation of the unconverted gases (G.P. 235421), and then a patent covering the use of pure iron as a catalyst (G.P. 247852). By 1909–10 the Badische had taken a more active part in the development of the synthetic process and the work of Bosch, Mittasch and other Badische staff led to the erection of an experimental unit at Ludwigshafen in 1910. The report of Haber and Le Rossignol to the Badische in 1909–10 is summarised in Z. Elektrochem. 1933, **19**, 53. The experimental unit was followed shortly by a full-scale plant at Oppau adjacent to Ludwigshafen, the construction of which started in 1911 and which commenced operations in September 1913, with a capacity of about 6,500 metric tons of nitrogen per year. The plant was greatly enlarged during the World War. The increasing demand for nitrogen in Germany during the war, the need for a factory less vulnerable than that of Oppau and the desire to exploit cheap brown coal led to the construction of a still larger synthetic ammonia works at Leuna, near Merseburg, in the brown coal region of central Germany. Construction was started in May 1916, and ammonia produced there in the early summer of 1917. The initial capacity of the plant was about 27,000 metric tons of nitrogen per year and was increased to about 120,000 metric tons within a year. Serious labour troubles and coal shortage after the war delayed the further enlargement of the plant, but its capacity was raised to 230,000 metric tons (tonnes), in 1925, to about 300,000 tonnes in 1926, and in 1928 it was producing at the rate of about 1,400 tonnes of NH_3 per day, corresponding to rather over 400,000 tonnes of fixed nitrogen per year. The present annual capacity of Oppau and Leuna is between 900,000 and 1,000,000 tonnes of nitrogen. In England, research work carried out under the auspices of the Ministry of Munitions culminated towards the end of the war in a project to build a synthetic ammonia plant at Billingham-on-Tees to operate a modified form of the Haber-Bosch process, a project which was abandoned when the war came to an end. After the war the site was bought by Messrs. Brunner, Mond & Co., Ltd., and a plant was built and started in 1923 with an annual capacity of about 10,000 tonnes per year of nitrogen. The plant has since been increased to a capacity of about 200,000 tonnes per year of nitrogen.

The World War stimulated research on the synthetic ammonia process in every country and there are now very few countries of any size which have not a synthetic ammonia works. A number of modifications of the original Haber-Bosch scheme have been evolved, principally the Casale, Claude, Fauser, Mont Cenis and N.E.C. (Nitrogen Engineering Corporation) processes. These differ from the Haber-Bosch and from one another in respect of the pressure and temperature employed for synthesis, the catalyst, or the method of removing ammonia from the system. The source of hydrogen, the method of separating the oxygen from the nitrogen of the air and the method of purifying the hydrogen and nitrogen also differ considerably among the installed plants and processes.

It is estimated that in 1932–33 the synthetic ammonia capacity represented by the Haber-Bosch process was 53%, by Casale 16%, Fauser 11%, Claude 8%, N.E.C. 5%, Mont Cenis 6%, Japanese (Showa Miryo) 1%. Of the total world's capacity in 1932–33 of nearly three million tons of ammonia-nitrogen (2,835,810 metric tons) only about 43% is at present in production (1935) and the percentage of processes actually in operation may differ considerably from the above.

By countries, Germany held 44% of the world's nitrogen capacity, U.K., U.S.A., and Belgium 8% each, France and Japan 7% each, Netherlands and Norway 4% each, Italy 3%, rest of the world 7%.

The Ammonia Equilibrium.—In 1903–04 Haber and Van Oordt commenced their experimental study of the ammonia equilibrium and published two papers, in 1904–05 (Z. anorg. Chem. 1904, **43**, 111 ; 1905, **44**, 341), describing experimental work done at one atmosphere pressure, using iron and nickel as catalysts. At 1,020°C. equilibrium was reached with 0·012% NH_3 by wt. in the gas mixture. Concentrations at other temperatures were calculated.

Nernst and Jost, stimulated by the disagreement between the calculated figures of Haber and those which would have followed from Nernst's heat theorem, undertook an examination of the ammonia equilibrium at atmospheric pressure and also at pressures up to 70 atmospheres in the temperature range 700°–1,000°C. Their results were published in 1907 and 1908 (Nernst, Z. Elektrochem. 1907, **13**, 521 ; 1908, **14**, 373 ; Jost, Z. anorg. Chem. 1908, **57**, 414).

In the meantime Haber and Le Rossignol had carried out a new set of measurements, firstly at atmospheric pressure in the range 700° to 1,000°C. (Ber. 1907, **40**, 2144) and secondly at pressures up to 30 atmospheres (Z. Elektrochem. 1908, **14**, 181).

Finally, a detailed series of determinations by Haber and his co-workers from 1914 to 1915 extended the temperature range down to 560°C., the maximum pressure covered being still 30 atmospheres (Haber, Z. Elektrochem. 1914, **20**, 597 ; Haber, Tamaru, Ponnaz, Greenwood and others, *ibid.*, 1915, **21**, 89, 128, 191, 206, 228, 241).

Later work at the Fixed Nitrogen Research Laboratory in Washington, U.S.A., by Larson and Dodge (J. Amer. Chem. Soc. 1923, **45**, 2918 ; Larson, J. Amer. Chem. Soc. 1924, **46**, 367) widened the range of measurements down to 350°C. and up to 1,000 atmospheres. Claude in 1919 also published equilibrium data for very high pressures (Compt. rend. 1919, **169**, 1039).

Fig. 3 gives the percentage of ammonia in equilibrium in a 3 : 1 hydrogen-nitrogen mixture at temperatures from 200° to 700°C. and pressures up to 1,000 atmospheres. The curves are derived from the above-mentioned work of Larson. For the equilibrium constant, the equation derived by Haber is :

$$\mathrm{Log}_{10}\,Kp=\log\frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}}\times p_{H_2}^{\frac{3}{2}}}$$

$$=\frac{2098\cdot2}{T}-2\cdot509\log T-1\cdot006\times10^{-4}T+1\cdot859\times10^{-7}T^2+2\cdot10,$$

or approximately, $\log_{10}Kp=\frac{2888}{T}-6\cdot134.$

Other equations are derived by Partington and Shilling ("Specific Heats of Gases," Benn, 1924) and by Gillespie (J. Amer. Chem. Soc. 1926, **48**, 28).

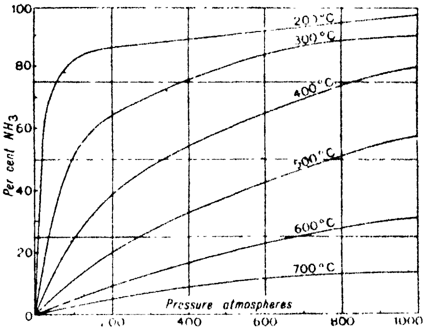


FIG. 3.

For very high pressures (up to 1,000 atm.), Larson derives the following (J. Amer. Chem. Soc. 1924, **46**, 370) :

$$\log_{10}Kp=\frac{2074\cdot8}{T}+2\cdot4943\log T+aT+1\cdot8564\times10^{-7}T^2+C$$

where a and C have the following values :

p. atm.	a	C
300	$-1\cdot256\times10^{-4}$	2·206
600	$-1\cdot0856\times10^{-3}$	3·059
1,000	$-2\cdot6833\times10^{-3}$	4·473

Catalysts for Ammonia Synthesis.—The early catalyst patents of Haber cover the use of osmium and a uranium–uranium carbide mixture. The many patents which followed have covered a wide range of materials, including with the above, iron, nickel, cobalt, molybdenum, manganese, magnesia, alkaline earth ferrocyanides, titanium, tungsten, etc. Patents have also been issued covering the addition to iron catalysts of "promoters," such as alumina, silica, zirconium dioxide, titania, etc., and also the addition of combinations of such oxides as alumina or silica with alkaline oxides such as sodium or potassium oxide.

The majority of synthetic ammonia plants in operation to-day make use of promoted iron catalysts, obtained by burning iron to form Fe_3O_4, mixing promoters with the fused oxide, and reducing the latter, when cooled and crushed, with the hydrogen-nitrogen mixture. Natural magnetite is sometimes used as a source of Fe_3O_4. The ferrocyanide catalyst used in the Mont Cenis process (*see below*) has been shown by Mittasch, Kuss, and Emert (Z. Elektrochem. 1928, **34**, 829) to consist essentially of α-iron, the cyanides and carbides formed therefrom having no effect in ammonia synthesis.

Very little published data are available on the relative activities of the various materials specified in patent literature, but a valuable comparison has been made by Larson and Brooks (Ind. Eng. Chem. 1926, **18**, 1305) of the activities of mixtures of iron, cobalt, nickel, tungsten and molybdenum. Iron is by far the most promising material of those given.

The activity of iron catalysts is enhanced by the addition of difficultly reducible oxides such as alumina, silica or zirconia. Larson showed *e.g.*, that at 450°C., 100 atm., and 5,000 space velocity (*i.e.* 5,000 volumes of gas per hour, measured at 0°C. and 760 mm., per unit volume filled with catalyst) an iron catalyst which normally produced 3–5% NH_3 from a 3 : 1 hydrogen-nitrogen mixture would produce 8–9% NH_3 when promoted with a few per cent. of alumina.

The addition of one of the above oxides is still more effective if an alkaline oxide such as sodium or potassium oxide is also added (Larson, Ind. Eng. Chem. 1924, **16**, 1002 ; U.S.P. 1489497 ; Almquist and Crittenden, Ind. Eng. Chem. 1926, **18**, 1307 ; Lachinof and Telegin, J. Chem. Ind. Moscow, 1934, **12**, 31).

The activity of ammonia catalysts is adversely affected by a number of so-called "catalyst poisons," of which the most commonly encountered in practice are sulphur compounds such as hydrogen sulphide, carbon oxysulphide, etc., and oxygen compounds such as water vapour, carbon monoxide, carbon dioxide or free oxygen. These are present in the hydrogen produced by most industrial methods and, although reduced to a minimum by intensive purification, are probably also present in minute traces in practically all ammonia synthesis systems. The loss in catalyst activity which results from an increase in concentration of any of the above poisons in the mixture of nitrogen and hydrogen passed over the catalyst is largely temporary in the case of oxygen compounds, that is, if the concentration of the poison is reduced again the initial activity of the catalyst is almost completely restored. This is true only if the period of "poisoning" has not been too prolonged. Poisoning by sulphur compounds is, however, cumulative and the initial activity is in general not recovered.

Special precautions for the removal of catalyst poisons are taken in practically all ammonia synthesis plants (*see below*). The effect of catalyst poisons on activity is examined by Larson (Chem. and Met. Eng. 1922, **26**, 683).

Mechanism of Ammonia Catalysis.—The most plausible theory so far advanced for the mechanism of ammonia catalysis postulates the activated adsorption of nitrogen on the surface of the catalyst with the possible subsequent formation on the surface of a nitride, or dissociation of the nitrogen molecules into atoms. The active nitrogen (or nitride) is then reduced by hydrogen adsorbed also on the catalyst surface in active condition, to form ammonia. The extent of the adsorption of nitrogen appears to be the limit to the activity of ammonia catalysts.

The function of catalyst promoters is not too clear. That such promoters as Al_2O_3 tend to retard the growth of large iron crystals (or "sintering") is now generally held, although another function of the promoter may be to increase the rate of activated adsorption of nitrogen. It has been shown fairly conclusively that the ammonia catalyst used in most synthesis processes consists of small crystals of α-iron, probably between 100 and 100,000 *mμ* (Almquist and Black, J. Amer. Chem. Soc. 1926, **48**, 2814 ; Wyckoff and Crittenden, *ibid.* 1925, **47**, 2866 ; Kobosew, Jerofejew and Sluchowsky, Z. Elektrochem. 1935, **41**, 274).

Hydrogen Production and Purification.—According to Waeser (Zentr. Kunstdünger Ind. 1931, p. 153) 52·4% of the hydrogen used in ammonia synthesis is made from water-gas, 29·1% by the fractionation of coke-oven gas, 17·0% from the electrolysis of water, and 1·5% from brine electrolysis, fermentation processes, natural gases, etc. (*see also* Curtis, "Fixed Nitrogen," 1932). For a full description of the various hydrogen-producing processes the article HYDROGEN should be consulted. They will, however, be briefly described here.

In the *Water-gas Process* the reduction of steam by carbon to form hydrogen and carbon dioxide, a reaction which proceeds only partially in the water-gas generator, is completed by causing the CO in the water-gas to react with steam at 450°-600°C. by passage over a catalyst, usually promoted iron oxide. The carbon dioxide is scrubbed out with water under a pressure of 10–55 atmospheres in counter-current scrubbers, and the gas is then compressed to the final synthesis pressure—in the Haber-Bosch plants, which all use the water-gas process, 200–250 atmospheres—the CO being then removed practically completely by scrubbing with ammoniacal cuprous formate or carbonate (or a mixture of both).

After this scrubbing process the gas contains 0·01–0·05% carbon monoxide and dioxide, 0·5–1% methane, argon, etc., and traces of ammonia, water vapour, and sulphur compounds. In some plants the gas is further treated with an ammonia or caustic soda wash to remove the last traces of carbon dioxide.

When ammoniacal cuprous formate solution is used, however, this treatment is not essential, but it is still necessary to remove catalyst poisons from the gas. Traces of moisture are removed by refrigeration at synthesis pressure—in the majority of plants, where the synthesis is carried out in a circulating system, the so-called "make-up" gas is admitted to the circulating gas at a point where the latter is refrigerated to remove synthesised ammonia. The traces of ammonia and moisture in the "make-up" gas are both removed in this way.

Traces of carbon monoxide are still present after the scrub with ammoniacal cuprous formate, and also traces of sulphur compounds. The latter arise from the organic sulphur compounds such as carbon oxysulphide which are present in the original water-gas. The hydrogen sulphide initially present in the water-gas is removed either before the CO conversion plant or at the CO_2 removal plant. Most of the organic sulphur compounds are converted to H_2S in the CO conversion plant, the H_2S being then removed during CO_2 removal, but conversion is not complete, and the traces of organic sulphur left behind are sufficient to cause serious catalyst poisoning.

These impurities are removed by passage through a "guard" converter or "purifier" before the make-up gas is allowed to enter the main synthesis system.

The *Electrolytic Process* produces hydrogen which is particularly free from deleterious impurities. Traces of oxygen (0·1–0·5%) are present. These were originally removed in the Fauser process by combining with hydrogen, using platinised asbestos as a catalyst, but in the later Montecatini plant at Merano a copper deoxidiser is used.

The *Coke-oven Gas Liquefaction Process*, which consists essentially in the separation of hydrogen from coke-oven gas by the fractional liquefaction of the other constituents—ethylene, methane, and carbon monoxide—produces also a relatively pure gas which requires no further purification. Traces of carbon monoxide remain in the gas, however, and must be removed by the use of a guard converter.

Although it is common to find, for example, the water-gas catalytic process used for making hydrogen in conjunction with the Haber-Bosch synthesis process, there is no essential connection between the various hydrogen processes and those for synthesis. Each of the above three processes for making hydrogen has its advantages in certain localities depending on the availability and price of coke, electric power and coke-oven gas, and can equally well be used in any of the standard synthesis plants.

Nitrogen Production and Purification.—Practically all the nitrogen used in the synthesis of ammonia is produced from the air, and the method used for removing the oxygen from the air to produce nitrogen depends generally on the method of hydrogen production employed.

Where the water-gas process is in use, as in Haber-Bosch plants, the nitrogen is obtained from producer gas, which is mixed before the CO conversion plant with water-gas in the required ratio.

In the coke-oven gas liquefaction process liquid nitrogen is commonly employed to wash out the last traces of methane and carbon monoxide, and by adjusting the temperature of this nitrogen wash the necessary 3 : 1 ratio of hydrogen to nitrogen is obtained.

To supplement electrolytic hydrogen, nitrogen from air liquefaction is commonly employed, although in some plants a nitrogen burner is used, in which hydrogen is burnt in air to produce the 3 : 1 hydrogen-nitrogen mixture.

Synthesis Processes.—As stated above, the original Haber-Bosch process has been modified in a variety of different ways, the resulting modifications, some slight and some quite radical, having given rise to a number of patented processes. Of these the most significant are the Casale, Fauser, Claude, Mont Cenis and American processes. Naturally enough, the processes are susceptible of considerable modification from plant to plant. All the above processes have this in common, that a mixture of nitrogen and hydrogen is passed through a bed of catalyst in a vessel (known as a "converter") capable of withstanding the necessary temperature and pressure. In most of the processes the unconverted gas is recirculated, after removal of the ammonia formed and addition of fresh nitrogen and hydrogen to replace that which has been consumed in making ammonia. In the Claude process the nitrogen-hydrogen mixture is exhausted by passage through a number of converters in series. The processes employ considerably differing pressures: the factors governing the choice of pressure are (*a*) the increase in conversion, and hence diminished recirculation (with certain other advantages), which follow higher pressure ; (*b*) the decreased volume of the gas at higher pressure ; (*c*) the increased wall-thickness, and hence cost, of vessels and pipelines with increased pressure ; (*d*) the increased cost of compression of the make-up gas with increasing synthesis pressure. These are reflected in capital and operating cost, and the aim in all plants has been to arrive at the optimum pressure at which the sum total of costs is at a minimum. Opinion on the subject obviously varies widely, since pressures vary between 200 and 1,000 atmospheres, but it would appear that the costs of most of the established processes are not greatly different and that the pressure factor is either not important or is outweighed by other considerations.

As will be seen from the equilibrium curves in Fig. 3, the lower the temperature at which a converter can be run, the higher is the possible conversion of nitrogen and hydrogen to ammonia. On the other hand, the reaction velocity with any given catalyst diminishes markedly with temperature. In practice, then, a compromise is made, and the converter is in general operated at such a temperature that the ammonia concentration in the exit gas is at a maximum. Most of the established processes work between 450° and 600°C. ; the Mont Cenis process works at a rather lower temperature, about 400°C. As Fauser and others have shown (*see below*), it is desirable for maximum conversion that the temperature gradient in the catalyst bed should fall steadily, so that the bulk of the conversion is made at a high temperature and therefore high velocity, and the final approach to equilibrium made under more favourable low-temperature conditions. In certain converters, such as those of Fauser and Casale, definite efforts are made to correct the natural tendency of the exothermic reaction to produce a rising temperature gradient in the catalyst bed.

The space velocity is a matter which should also be discussed. As the space velocity (*i.e.* the volume of free gas passed through unit volume of catalyst per hour) increases, so the approach to equilibrium becomes less favourable ; on the other hand, the total amount of ammonia made in a given apparatus will increase. The actual space velocity used is again a matter of compromise between a number of factors, and it is probable that most processes are using space velocities of 40,000 or less.

The Haber-Bosch process, as operated by the I.G. at Oppau and Leuna, in Germany, and by the I.C.I. at Billingham, England, will first be described, and the essential differences of the other processes will then be indicated.

Haber-Bosch Process.—The working of the Haber-Bosch process is illustrated diagrammatically in Fig. 4. The process operates at 200–250 atm. pressure; the nitrogen-hydrogen mixture, obtained from water-gas and producer gas and purified as described above, passes from the **CO** removal plant through a "guard" converter or "Vorofen" G into the circulating synthesis system. The function of the guard converter is to convert the final traces of carbon monoxide and carbon dioxide to methane, and to absorb the last traces of sulphur compounds. The guard converter is in general of similar design to the main synthesis converters, although the heat exchange apparatus may differ somewhat; the catalyst used is also of similar composition and is frequently spent catalyst from the main synthesis converters. The guard converter may or may not be run to synthesise ammonia; if operated at about 350°–400°C it is still effective in purification and more economical in heat consumption. If the concentration of sulphur compounds in the make-up gas is sufficiently high, the activity of the catalyst in the synthesis reaction is rapidly destroyed, but although inactive in ammonia synthesis it will still operate as a purifier.

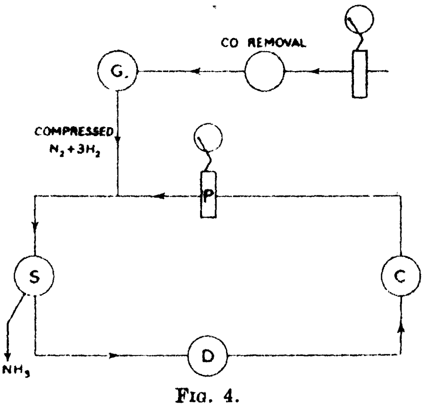


Fig. 4.

The circulating system consists of a number of converters C, in which a proportion of the nitrogen and hydrogen is combined to form ammonia; ammonia scrubbers S, in which the ammonia is scrubbed out with water; gas-drying plants D, in which most of the water vapour and residual ammonia are removed, and gas circulators P, which boost the circulating gas to a pressure necessary to overcome the pressure drop through the circulating system. The make-up gas enters before the ammonia scrubbers, in order that any ammonia synthesised in the guard converter, together with water made in converting **CO**, may be removed.

Ammonia solution is released from pressure at the base of the scrubbers. According to requirements, part of the make may be obtained as gas after this release and part as a solution, or the whole may be obtained as a solution of any desired strength.

The inert constituents derived from the make-up gas—argon and methane—accumulate in the circulating system and are maintained at an economic level by purging, *i.e.* blowing off the synthesis gas intermittently or continuously. The purge gas can be used for fuel purposes. The ammonia content of gas leaving the synthesis converters is commonly 8–10%.

The converter consists of a thick-walled forging of tungsten or nickel-chrome steel, closed at each end with a large plug or nut, and holding (*a*) a catalyst basket and (*b*) a heat exchanger. Supplementary external heat exchangers are sometimes used. The whole is lagged internally and it is common practice to cool the inside of the forging wall with part of the incoming gas in order to minimise hydrogen attack and decarburisation of the steel. The heat exchanger is adequate to make the apparatus as a whole "autothermic," *i.e.* self-supporting in heat when in normal operation, the heat evolved in the reaction (13,000 kg.-cals. per kg.-mol. of ammonia formed) being sufficient to compensate for radiation losses from the forging plus the heat carried away by the gases leaving the apparatus. It is necessary, however, to supply heat initially in order to raise the gas and catalyst to reaction temperature, and this is normally effected by an electric heater above the catalyst container.

The temperature in the catalyst bed is maintained at 450°–600°C. The Haber-Bosch process and plant have undergone progressive development since the inception of the process in 1913, and have been considerably modified and improved in application to other factories. There is nowadays much less difference than is commonly supposed between this process, as operated in modern plants, and the rival processes outlined below. The Leuna plant of the I.G. is described by J. R. Partington in J.S.C.I. 1921, **40**, 144R, by Combi in Giorn. Chim. Ind. Appl. 1921, **3**, 199, and by Voigtlander in Z. Komp. u. Fluss. Gas, 1926, **25**, 3.

Casale Process.—The process patented by the late Luigi Casale of Italy operates in the region of 650–750 atm. A circulating system is used, similar to the Haber-Bosch process, but ammonia is removed as anhydrous liquid by direct external cooling with water followed by refrigeration. The mean operating temperature is 500°C., and the gases leaving the converter are said to contain 15% of ammonia at 12,000 space velocity (*i.e.* 12,000 volumes of free gas per hour per unit volume of catalyst). Sufficient ammonia is left in the gas returned to the converter to make the reaction slightly endothermal and thus to avoid overheating the catalyst. An electric heater then makes up the slight deficiency in heat; in practice the heater is kept on constant load and the rate of circulation varied to maintain temperature.

The Ostend plant of the Union Chimique Belge, using hydrogen from coke-oven gas, is described by Pallemaerts in the Report of the International Conference on Bituminous Coal, 1928, II, 178. It is there stated that the recirculation pump was to be replaced eventually by an injector, thereby simplifying the circuit and reducing maintenance costs, but this has not been put into effect on all Casale plants. A drawing of an early Casale converter is given in Curtis's "Fixed Nitrogen," p. 236; the internal wall of the forging is cooled by the cold incoming gas.

Fauser Process.—The Fauser process is similar in design and working details to the Haber-Bosch. The working pressure is generally about 300 atmospheres.

The Fauser converter includes a system of heat exchangers in the catalyst, by means of which the catalyst temperature is controlled and is made to fall steadily from 600° to 450°C. The resulting conversion is high, and the effluent gases contain about 15% NH_3. The ammonia is normally removed by cooling these gases with water, after which the removal is completed and the gases dried by refrigeration, the anhydrous ammonia removed in the water-cooled stage being employed to cool, by evaporation, the circulating gases.

In some plants ammonia is removed by water scrubbing, the separation of anhydrous ammonia being effected by distillation, utilising heat from the interchangers for the process.

The Fauser plant at Traill, British Columbia, is described by Kirkpatrick in Chem. Met. Eng. 1931, **38**, 626. The hydrogen at this plant is obtained by electrolysis of water, the last traces of oxygen being removed by passage through heated copper Raschig rings. A special oil separator is used after the circulator to remove the last traces of oil (which is a catalyst poison), before the gas enters the converter. The gases leaving the converter are said to contain about 12·5% NH_3. Other Fauser plants described in the literature are the Lutterade plant of the Dutch State Mines (Van Iterson in Iberica, 1933, No. 989) and the Sluiskill plant, also in Holland (Borelli, Chem. Met. Eng. 1932, **39**, 126), both of which plants use hydrogen from coke-oven gas (*see also* G. Fauser, Giorn. Chim. Ind. Appl. 1931, **13**, 361).

Mont Cenis Process.—This process was developed in 1926–27 in the Ruhr district, principally with the object of utilising waste coke-oven gas. The I.G. at that time held numerous basic patents, in particular those for ammonia synthesis above 100 atmospheres, and research work was therefore devoted to the finding of a catalyst which would work effectively outside the I.G.'s protected range. The search was successful, and Uhde and his co-workers developed a catalyst giving 12–13% NH_3 at pressures less than 100 atmospheres and at 400°C. The catalysts covered by the various patents (B.P. 247225, 253122, 273735, 305753) are ferro- and ferricyanides of metals in the iron group, in particular iron and aluminium. Subsequently, patent litigation with the I.G. revealed that the ferrocyanide catalysts are, effectively, α-iron, as are the more usual iron catalysts derived from the reduction of Fe_3O_4.

In the Mont Cenis process, as applied in the Ruhr and in the Shell plant in California, a circulating system is used. The hydrogen-nitrogen mixture obtained from coke-oven gas liquefaction (in the Shell plant by reforming natural gas, *i.e.* by cracking) is freed from traces of CO (0·05–0·02%) and oxygen by a guard converter, using a nickel catalyst at 300°C. The make-up gas and cooled circulating gas from the synthesis converters—containing ammonia—then pass together through the ammonia removal system, consisting of interchangers and refrigerator, in which the gas is cooled by evaporating liquid ammonia. 0·2–0·5% of ammonia is left in the gas, which then passes to the synthesis converters, where the catalyst is maintained at an even temperature of 400°C. The gas leaving the converter is said to contain 8–13% of ammonia, depending on the age of the catalyst; this gas is cooled with water, thus separating ammonia as liquid, before passing on to the refrigeration section (Scholvien, Chem. Met. Eng. 1931, **38**, 82).

Claude Process.—The Claude process is unique, in that it employs a train of converters in series, with no recirculation system as in the Haber-Bosch and other processes. The pressure employed is high, 900–1,000 atm., and the conversion of nitrogen and hydrogen correspondingly high. After passage through four sets of converters in series, only 10–20% of the initial nitrogen and hydrogen is left unconverted.

In actual practice, with converter temperatures between 500° and 650°C. the exit gas from the first converter contains 25–40% NH_3. The yield of ammonia per kg. of catalyst per hour is said to be about 6 kg. compared with 0·3 or 0·4 for the Haber process. Converter design is therefore such as to dissipate heat and in the earlier Claude converters there was little attention paid to heat interchange and the design was very simple. More recent designs employ an internal interchanger. The original Claude converters were made of special steel to resist the high temperature to which they were exposed, steels of the B.T.G. type (11% Cr, 61% Ni, 1·3% Mn, 2·2% W) being used. In later designs the wall is cooled internally and steel forgings are used. A guard converter or purifier using spent catalyst and working at 400°C. leads the train of converters, after which there are four sets in series, the first set consisting of two converters in parallel, and the others of one converter only (Fig. 5). Each

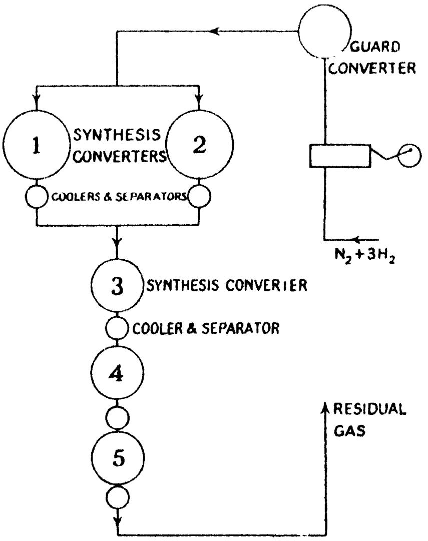


Fig. 5.

converter has its own cooler, in which liquid ammonia separates out at about 20°C. into a separator, and may be followed also by a refrigerator.

The residual gas leaving the last converter is returned to the coke-oven gas purification section (the Claude plants normally obtain hydrogen from coke-oven gas), or may be used as a fuel.

The Claude plant at Béthune is described by Scott in the Colliery Guardian, 1924, **127**, 737.

American Processes.—A modification of the Haber-Bosch process has been worked out by the Fixed Nitrogen Research Laboratory in Washington, U.S.A. Full details of this process are published in the technical literature (Chem. Met. Eng. 1924, **30**, 948).

A diagram of the converter is reproduced in Fig. 6 and provides a typical example of an ammonia synthesis converter. The entering hydrogen-nitrogen mixture passes up (and cools) the wall of the forging at 1, and enters the heat exchanger 2. It travels through the central tube 3 with electric heater for starting purposes, and thence through three concentric catalyst chambers 4, 5, and 6. The arrangement is said to result in an even temperature distribution through the catalyst, operating between 450° and 500°C. Other novel features are the use of a guard converter deliberately forming ammonia, the liquefaction of which itself serves to purify the gas ; the use of liquid ammonia instead of oil as a lubricant on the circulating pump to avoid contamination of the circulating gas with oil. The catalyst, it is claimed, will work at 450°–500°C. for many months without renewal. The process has been worked in several small units but in no very large installation.

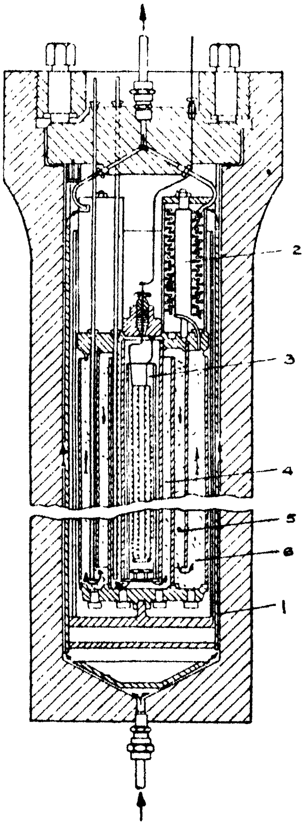


Fig. 6.

The plants built by the Nitrogen Engineering Corporation also make use of a modified Haber-Bosch process, working at 300 atmospheres.

Recent Developments in Ammonia Synthesis.—Experiments recently carried out by Basset (Bull. Soc. chim. 1935 [v], 2, 108) at very high pressures, up to 4,500 kg./cm.^{2} (about 4,360 atmospheres), have given some interesting results. He finds that at pressures of this order, ammonia synthesis takes place in the absence of a catalyst and in the presence of a considerable percentage of impurities. At 4,500 kg./cm.^{2} and a temperature of 850°C. the conversion of nitrogen and hydrogen to ammonia in the absence of catalyst is substantially complete (97%), at 2,000 kg./cm.^{2} is 40% complete, and 1,000 kg./cm.^{2} only 3%. It is claimed that the fact of being able to dispense with a catalyst means that impure gas can be used with no harmful effect on yield. The researches have not so far been carried beyond the laboratory stage.

II. MANUFACTURE OF AMMONIA BY THE DESTRUCTIVE DISTILLATION OF COAL, LIGNITE, ETC.

Ammonia is obtained as a by-product when nitrogenous organic matter, in particular coal, peat, and shale, is subjected to the process of destructive distillation. The greater proportion is obtained in the manufacture of town-gas, power gas or coke from coal ; a small quantity is obtained in the distillation of shale for the production of shale oil, and some is recovered from the gases evolved in blast-furnaces where coal is used direct as fuel.

Statistics of the world production of nitrogen as by-product ammonia are given on p. 331, and figures for production in England and Wales on p. 332.

Of the total world production of by-product ammonia, about 18% came from the U.K. in 1929, 23% from Germany, 36% from the U.S.A., 6% from France, 6% from Holland and Belgium, and 11% from the rest of the world.

Coke for metallurgical purposes was formerly manufactured in beehive ovens and no recovery of by-products attempted, but these have been largely superseded by by-product coke ovens, the ammonia production from which is comparable in quantity with that from gas-works.

Competition from the synthetic product has been so severe in recent years that many gas-works and coke ovens have ceased to recover ammonia. This is particularly true of the smaller works, although there is a certain tendency to manufacture sulphate centrally from ammonia liquor supplied from a number of small works.

Nitrogen Content of Coal.—Coal, being of vegetable origin, contains nitrogen, although the element is present in somewhat greater quantity than in fresh vegetable matter. The percentage of nitrogen found in coal varies between 1 and 3%, the average nitrogen content of bituminous coals being about 1·4%.

Foster (Proc. Inst. Civ. Eng. 1884, **77**, iii, 23) found :

In Welsh anthracite .	0·91% N.
In English coals . .	1·66 to 1·75% N.
In Scotch cannel . .	1·28% N.

Schilling (J. Gasbeleucht. 1887, **30**, 661) using the Kjeldahl method of estimation, found 1·06 to 1·50% N in a number of German coals, 1·45% in an English (Bolton gas) coal, 1·49% in Pilsener cannel coal, and 0·52% in Bohemian lignite. McLeod (J.S.C.I. 1907, **16**, 137) analysed 80 samples of Scottish coals and cannels, and found percentages of nitrogen varying from 0·91 to 1·87%, and averaging 1·43%.

Ammonia from Coal Distillation.—The yield of by-product ammonia represents, however, only about one-sixth of the nitrogen originally present in the coal. The theoretical yield of nitrogen per ton of coal, if all the fixed nitrogen were recovered, is about 31 lb., while the average yield of ammonium sulphate in gasworks and by-product coke ovens is 25–27 lb. per ton, or about 5·5 lb. of nitrogen per ton. This is due in the main, not to inefficient operation, but to the fact that when coal is carbonised only a fraction of the nitrogen present in the coal is evolved as ammonia, the remainder being distributed amongst the other products—coke, gas (as free nitrogen), tar, and cyanide.

The distribution of nitrogen amongst the different products of destructive distillation varies considerably, being dependent both on the nature of the coal and on the conditions of carbonisation ; the rate at which carbonisation proceeds, the type of retort used, and especially the temperature employed have a marked influence. In low-temperature carbonisation processes, operating at temperatures of 450°–600°C., a very large proportion of the nitrogen remains behind in the coke. In ordinary high-temperature processes, where temperatures of the order of 1,000°C. are used, more nitrogen is given off from the coke. Although this may be primarily in the form of ammonia it is partly converted into HCN by the action of incandescent coke and partly dissociated into its elements, the dissociation taking place to an increasing extent when the gases evolved pass over heated surfaces.

Ammonia is one of the first products of distillation, the evolution of ammonia from heated coal commencing at temperatures between 300° and 400°C., and continuing up to 540°C., when the evolution of ammonia (sometimes called " primary " ammonia) ceases. Within the range 540° to 870° very little more ammonia is evolved, but above 870°C. further appreciable quantities appear (" secondary " ammonia).

The maximum yield of ammonia is obtained between 900° and 950°C.

The following table, due to Simmersbach (Stahl u. Eisen, 1914, **34**, 1153, 1209), shows the distribution of the total nitrogen amongst the various products of carbonisation in an Upper Silesian coal containing 1·4% N. The results are from small-scale experiments.

PERCENTAGE OF NITROGEN IN VARIOUS PRODUCTS BASED ON DRY ASH-FREE COAL.

Temp. °C.	In coke.	N_2 in gas.	As NH_3.	In tar.	As HCN.
600	71·69	18·13	7·81	2·12	0·25
700	65·43	12·13	18·13	3·65	0·66
800	63·65	10·73	21·28	3·47	0·87
850	61·12	10·37	23·68	3·72	1·11
900	58·40	12·14	24·12	4·15	1·19
1,000	49·98	21·53	23·15	4·11	1·23
1,100	41·39	30·51	23·09	3·70	1·31
1,200	26·43	45·10	22·84	4·21	1·42

The following tables, which give figures obtained over a long period of working in gasworks and coke ovens respectively, represent fair averages for the two industries, although the increasing tendency towards the use of coke ovens in gasworks will affect the validity of McLeod's figures for the gas industry as a whole. The gasworks figures are given by McLeod (J.S.C.I. 1907, **26**, 137) as the result of working at the Govan Gasworks, Glasgow, and the coke oven figures by Short (*ibid.* 1907, **26**, 581) for the working of Otto-Hilgenstock coke ovens on Newcastle coal.

	In coke.	N_2 in gas.	As NH_3.	In tar.	As HCN.
Gasworks .	58·3	19·5	17·1	3·9	1·2
Coke ovens .	43·3	37·1	15·2	3·0	1·4

The distribution of nitrogen in the products from continuous vertical retorts is shown in the following table, the data for which were obtained in tests done by the Gas Investigation Committee (Proc. Inst. Gas Eng., June, 1920).

Coal charge	In coke.	N_2 in gas (and lost).	As NH_3.	In tar.	As HCN (and cyanogen).
unsteamed	60·1	13·2	17·9	6·8	2·0
Steaming, 32·7 lb. steam per 100 lb. coal .	49·7	20·0	19·5	8·9	1·9

The normal yield of ammonia from high-temperature horizontal retorts or coke ovens is, as stated above, 25–27 lb. of sulphate per ton of coal. Many attempts have been made to increase the yield, such as the Cooper process involving the addition of lime to the coal before carbonisation (B.P. 5713, 1882). Salmang (Z. angew. Chem. 1919, **32**, 148) has also shown that the addition of chalk or iron oxide to the coal increases the ammonia yield, and that the passage of steam and air through the fuel bed increases the yield. None of these attempts has met with any permanent success; the Cooper process was tried in a number of gasworks and abandoned, as the gain in ammonia yield was more than counterbalanced by drawbacks such as the depreciated quality of the resulting coke.

With the vertical retort, however, even working at a higher temperature, a higher yield of ammonia may be obtained in spite of the greater tendency to ammonia decomposition, because the volatile products escape more rapidly from the hot zone. The yield is still further increased by the common process of steaming the coal-charge to increase the water-gas production in the retort, and may then amount to 40–50 lb. of sulphate per ton of coal.

It has long been known that the nitrogen in coke can be completely converted to ammonia by combustion of the coke in steam (Grouven, Versuchsstationen J., **28**, 343; Beilby, J.S.C.I. 1884, **3**, 216), and the experiments of Salmang (Aachen, 1914, Dissertation; J.S.C.I. 1916, **35**, 346) and of Cobb (Gas J., Oct. 19, 1921; Fuel, 1922, **1**, 197) have demonstrated the important rôle of steam in ammonia formation under carbonisation conditions. Ammonia is formed by reaction between steam and coke at concentrations far in excess of those at which it would be in equilibrium with the nitrogen and hydrogen present; the subsequent decomposition of the ammonia can be largely prevented if the gases are removed sufficiently rapidly from contact with hot surfaces, and such decomposition is also greatly retarded by the presence of steam and hydrogen. Cobb and Hollings have demonstrated in small-scale experiments the effect of exposing the gases to prolonged heating. At 800°C., 22·5% of the nitrogen in the coal was recovered as ammonia if the gases were removed rapidly from contact with heated surfaces; the nitrogen recovered as ammonia fell to 17·2% when the gases were drawn through a heated tube and exposed to radiant heat, and to 9·4% if the gases were passed through heated coke (*see also* Mott and Hodsman, J.S.C.I. 1923, **42**, 4T, and Sommer, Stahl u. Eisen, 1919, 294, 349).

Processes for Ammonia Recovery.—Three types of process are in use for the recovery of ammonia in gasworks and coke ovens. In the first and second the ammonia may be recovered and sold, partly or wholly, as gas liquor or sulphate; in the third it is all recovered as sulphate (Fig. 7).

(1) The Indirect Process, in which the gas is cooled, thus condensing out tar, water, and some ammonia in solution, after which the gas is washed with water to recover the remainder of the ammonia. The ammonia liquor is then distilled into sulphuric acid.

(2) The Semi-Direct Process, in which the gas is cooled as above, condensing out tar and liquor, and is then passed direct into sulphuric acid. The condensed liquor is distilled into sulphuric acid as in (1), but there is considerable economy in the volume of liquor to be distilled.

(3) The Direct Process, in which the gas is passed directly into sulphuric acid, with no prior condensation of ammonia liquor. The use of a still is thus entirely avoided.

The first method, the indirect one, is by far the oldest and is used very extensively, particularly in gasworks. The semi-direct and direct processes have been developed and perfected within the last thirty years, largely in connection with coke ovens. The direct process is also employed, as will be seen below, in ammonia recovery from producer gas.

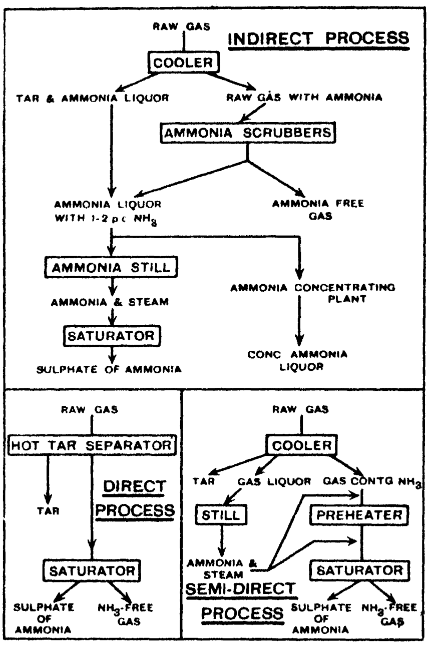


Fig. 7.

The three methods of recovering ammonia are discussed below in more detail (pp. 342–350).

Several processes have been devised in which the H_2S present in the gas is used to provide the sulphate radicle, in particular those of Feld (B.P. 3061, 1909; Z. angew. Chem. 1912, **25**, 705) and of Burkheiser (B.P. 20920, 1908; 21763, 1908; 17359, 1910).

Feld's name is associated with two processes, in the first of which (the "ferrous sulphate process") the gas is washed with ferrous sulphate solution, making ammonium sulphate and ferrous sulphide; the latter is then dissolved as tetrathionate by treatment with SO_2, and the solution of tetrathionate used to remove the remainder of NH_3 and H_2S from the gas, so reprecipitating the iron as FeS, which is again treated with SO_2 in a cyclic process. The reactions are:

$$FeSO_4+2NH_3+H_2S=(NH_4)_2SO_4+FeS$$
$$FeS+3SO_2=FeS_4O_6$$
$$FeS_4O_6+2NH_3+H_2S=(NH_4)_2S_4O_6+FeS$$

Part of the circulating solution is withdrawn from time to time and oxidised, whereby sulphates are obtained:

$$FeS+(NH_4)_2S_4O_6+O_2 \\ =FeSO_4+(NH_4)_2SO_4+3S$$

The sulphur is filtered off to supply the SO_2 required, and the ferrous and ammonium sulphates return for use in the first washing of the gas. Ammonium sulphate is removed by withdrawing part of the liquor as it accumulates and evaporating.

A somewhat similar process was later suggested by Cobb, using zinc sulphate instead of ferrous sulphate. The zinc sulphide from the first reaction is roasted, yielding ZnO and SO_2, and $ZnSO_4$ then reformed by blowing the roaster gases, containing SO_2 and O_2, through a suspension of the ZnO in water :

$$ZnSO_4+2NH_3+H_2S=(NH_4)_2SO_4+ZnS$$
$$2ZnS+3O_2=2ZnO+2SO_2$$
$$2ZnO+2SO_2+O_2=2ZnSO_4$$

Feld's second and later process, the "polythionate" process, employs a solution of ammonium tetrathionate, made originally from ammonium sulphide and SO_2. The solution absorbs H_2S and NH_3, and the spent solution is regenerated by SO_2:

$$4(NH_4)_2S_4O_6+6NH_3+3H_2O=5(NH_4)_2S_2O_3+2(NH_4)_2S_3O_6$$
$$(NH_4)_2S_4O_6+3H_2S=(NH_4)_2S_2O_3+5S+3H_2O$$
$$2(NH_4)_2S_2O_3+(NH_4)_2S_3O_6+2S+3SO_2=3(NH_4)_2S_4O_6$$

Thus in this process of alternate absorption and regeneration, ammonium tetrathionate builds up in solution. Part of the solution is withdrawn from time to time and boiled, giving ammonium sulphate, SO_2, and sulphur. The two last-named supply the SO_2 required for the reactions.

Feld's processes have suffered considerably from the war and from his death, but they are generally reputed to have proved too complicated in practice.

In Burkheiser's process H_2S is first removed from the gas by absorption in a special form of iron oxide, in small agglomerates, which is said to permit of relatively high through-puts. The ammonia is then removed by washing the gas with a solution of SO_2 giving ammonium sulphite. The SO_2 is obtained by regenerating the spent oxide with hot air at about 140°C. Ammonium sulphite thus builds up in solution, and finally separates out. The salt is filtered off and oxidised with hot air to sulphate in a special form of apparatus.

$$Fe_2O_3+3H_2S=Fe_2S_3+3H_2O$$
$$2Fe_2S_3+9O_2=2Fe_2O_3+6SO_2$$
$$SO_2+2NH_3+H_2O=(NH_4)_2SO_3$$
$$2(NH_4)_2SO_3+O_2=2(NH_4)_2SO_4$$

The Burkheiser process is said to be in use at the Tegel Gasworks, Berlin, but has never yet been successfully operated in this country.

Ammonia in Producer Gas Manufacture.—In the manufacture of producer gas from coal (*see* GAS, PRODUCER) by the simultaneous passage of air and steam through an incandescent fuel bed, substantially the whole of the carbon of the fuel is gasified together with the nitrogen it contains. Part of the nitrogen is recovered in the form of ammonia. The source of the ammonia is entirely the nitrogen in the fuel ; no successful attempt has so far been made to obtain ammonia by reaction between the nitrogen in the air blast and the hydrogen formed by reduction of the steam.

The ammonia recovered in producer gas may be regarded as formed in two ways, (*a*) by carbonisation of the coal, and (*b*) by interaction between the steam (or nascent hydrogen produced by reduction of the steam) and the nitrogen in the coke. The factors governing the formation of ammonia in both stages have been discussed to some extent above. In stage (*b*) (as already shown) the conversion to ammonia is governed partly by equilibrium considerations, *i.e.* the equilibrium

$$N_2+3H_2\rightleftharpoons 2NH_3,$$

but not by this entirely ; the ammonia produced during gasification is not in equilibrium with the nitrogen and hydrogen present, and the subsequent decomposition of the ammonia does not proceed to completion at the speeds with which the gases are normally removed from the hot zone. Decomposition of the ammonia is, furthermore, retarded considerably by the presence of steam.

In a given gas producer, the percentage of nitrogen recovered as ammonia increases markedly as increasing quantities of steam are used and, therefore, as the hydrogen content of the gas rises.

In practical tests carried out on a Mond producer by Bone and Wheeler (J. Iron and Steel Inst. No. 1, 1907) the percentage of the nitrogen in the coal obtained as ammonia rose from 26·5%, using 0·8 lb. steam per lb. of fixed carbon gasified, to 49%, using 2·64 lb. steam per lb. of fixed carbon gasified. The hydrogen content of the gas rose correspondingly from 16·6 to 22·65%. Further tests carried out on a similar producer by the Power Gas Corporation (Rambush, "Modern Gas Producers," Benn, 1923) raised the ammonia recovery up to 61·5%, using 4·24 lb. steam, and with a hydrogen content of 26·0%. The latter series of tests also demonstrated that the time factor is of importance, *i.e.* that with a longer time of contact between steam and coke high ammonia production can be maintained with a lower steam consumption. When the time of contact was doubled, the ammonia recovery increased from 49·0 to 60·0%, the steam consumption being maintained at about 2·6 lb. steam per lb. of fixed carbon gasified.

Sachs (Diss. Karlsruhe, 1913) demonstrated that the ammonia yield could be nearly doubled by rapidly chilling the gases as they left the hot zone.

A number of gas producers have been devised with the special object of recovering the maximum amount of ammonia. Of these the best known and most successful is the Mond gas producer, in which by using a high steam rate (85°C. air blast saturation temperature, or about 2·5 lb. steam per lb. of coal) upwards of 60% of the nitrogen in the coal is recovered as ammonia. The air and steam are preheated to 180°–250°C., to enable a high steam consumption to be maintained without undue decrease in the calorific value of the gas. Similar types of by-product recovery producer are the Duff, Crossley, and Lymn. The Moore and Power Gas processes offer high ammonia recovery with a lower steam consumption than the Mond process.

On account of the relatively large quantities of gas which have to be treated, ammonium sulphate is generally made directly by washing the producer gas with dilute sulphuric acid (containing circulating ammonium sulphate liquor). The solution is then evaporated and crystallised. Ammonium sulphate made from producer gas has generally a grey or brown tinge, due to the presence of traces of organic matter, originating from the tar.

Severe competition from synthetic ammonium sulphate in recent years has made by-product recovery less profitable, and many of the Mond installations in this country have either shut down or abandoned ammonia recovery.

Ammonia from Shale, Blast-Furnace Gas, Peat, etc.—In the distillation of shale for the production of shale oil, an industry which is particularly developed in Scotland (*see* PARAFFIN), ammonia is evolved and is recovered by methods similar to those used in gasworks. Scottish shales average about 0·6% nitrogen, of which about 60% is recovered as ammonia, giving a yield of about 35 lb. of sulphate per ton of shale.

The 1934 production of the Scottish shale industry was 25,240 tons of sulphate, or roughly 6,300 tons of nitrogen (Annual Report on Alkali Works, 1934).

The oil vapours, gases and steam pass from the retorts into condensers, where oil and ammonia liquor separate and the gas is then scrubbed with water to remove residual ammonia. The combined liquor is worked up into sulphate.

As in coal carbonisation, the use of steam increases very considerably the yield of ammonia and has no deleterious effect on the main product, which in this case is the oil. The addition of steam for increasing ammonia yields was, in fact, first worked out in the shale oil industry, chiefly by Young and Beilby (J.S.C.I. 1884, **3**, 216 ; J. Roy. Soc. Arts, 1885, **33**, 313 ; B.P. 1578, 1880 ; 1587, 1881 ; 2169, 1881 ; 4284, 1881 ; 1377, 1882 ; 5084, 1882).

The gas from blast-furnaces in which coal is employed as fuel contains ammonia and tar, which are removed from the gas before it is used as a fuel in gas engines or boilers. Iron-works recovering ammonia in this way are almost entirely confined to Scotland, since only there is coal found sufficiently hard for use in the blast-furnace without crushing. In England, with the exception of some parts of Staffordshire, hard metallurgical coke is used instead.

The total contribution to nitrogen production from this source is very small, being only 200–300 tons per year of sulphate (Annual Report on Alkali Works, 1934). It is stated by the above authority that the use of coal in blast-furnaces is being abandoned even in Scotland in favour of coke.

The tar and ammonia are recovered by methods similar to those employed in gasworks.

Enormous deposits of peat exist in the U.S.A., in Ireland, Germany and many other places, its nitrogen content is 1–2·5% and sometimes as high as 4% and many processes have been proposed to recover this nitrogen as ammonia, but very little success has been achieved on the large scale and no appreciable quantity of ammonia is now made this way. The lack of success is due in the main to the large quantity of water contained in the peat, which is costly to remove, and to the competition from other methods of making ammonia. The two most promising methods are those of Woltereck (B.P. 16504, 1904), in which air and steam are passed through peat at 350°–400°C., and of Mond, Frank and Caro (Z. angew. Chem. 1908, **21**, 1597), in which the Mond producer is used to gasify peat. Rambush (" Modern Gas Producers," Benn, 1923) describes a Mond ammonia recovery producer working on Italian peat and producing 111 lb. of sulphate per ton of dry peat, or about 60% nitrogen recovery. The utilisation of peat is also discussed in the Report of the Nitrogen Products Committee (M.I.D.), 1919.

Indirect Process for Ammonia Recovery.—The indirect process still so largely employed in gasworks and coke ovens will first be described in detail, after which the direct and semi-direct processes will be dealt with.

In the first-named process, as outlined above, the gas is first cooled. Tar and water vapour condense and the condensed water removes a large portion of the ammonia and some gaseous impurities from the gas, the remainder of the ammonia being then recovered by washing the gas with water. The ammonia removed by condensation alone in the so-called " virgin liquor " deposited in the hydraulic main and in the condensers, as distinct from that removed by the subsequent washing of the cold gas, is one-third to one-half of the total recovered (Meade's " Modern Gasworks Practice "). Hunt finds 42·7% removed in the virgin liquor, while Curphey (Alkali Report, 1926, p. 29) states that 50 to 60% is so recovered.

The various types of apparatus used for cooling and scrubbing the gases and the methods of operating these are described in the articles on GAS (COAL) and COKE.

Properties and Composition of Gas Liquor.—The ammoniacal liquor obtained by the cooling and washing of the crude coal gas in gasworks and coke ovens is, after separation from the tar by settling, a pale yellow or dark brown liquor. It smells strongly of ammonia, hydrogen sulphide and phenols. Its specific gravity usually varies between 1·01 and 1·03. The liquor is usually obtained in three stages, (*a*) in the hydraulic main, where the gas is cooled to 60°–70°C., and where the heavier tars are deposited ; this liquor is weak in total ammonia (0·5 to 1·0%) and particularly in the less stable ammonium salts such as sulphide and carbonate, as would be expected from the temperature at which it is formed; (*b*) in the condensers, where the gas is cooled to atmospheric temperature ; this is more concentrated, and contains 2–3·5% of total ammonia; (*c*) in the scrubbers and washers, where the cold gas is further scrubbed with water to effect complete removal of the ammonia ; the strength of this third liquor may vary considerably, depending on the construction and operation of the washing plant. The first two products together comprise the “ virgin liquor,” but the “ virgin liquor ” and the scrubber liquor are usually collected together with the tar in a common storage well or wells.

Frequently the hydraulic main liquor is circulated continuously and is also used, after cooling, in the preliminary washers or scrubbers, thereby reducing the amount of fresh water which must be used on the final scrubber.

Crude coal gas contains usually about 1·5% by volume of ammonia ; at the outlet from the condensers the ammonia content has been reduced to 0·75–1·0%. The yield of virgin liquor is usually about 10 to 14 gallons per ton of coal carbonised.

Not only does the quantitative composition of the ammoniacal liquor vary according to the stage in the process at which it is made, but that of the total gas liquor is dependent on the class of coal carbonised, on the conditions of carbonisation and on the construction and operation of the condensing and scrubbing plant. The qualitative composition, however, varies very little ; the primary products formed in the liquor are ammonium chloride, sulphides, carbonates and carbamate, and cyanide, all produced by reaction between ammonia and the acidic constituents of the crude gas, viz. hydrogen chloride, sulphuretted hydrogen, carbon dioxide, and hydrocyanic acid. The chloride is always concentrated in the earlier stages, being only present to any extent in the hydraulic main and condenser liquor. The carbonates, sulphides and cyanide, each having a considerable partial pressure of ammonia which increases with the temperature, are less concentrated in the hydraulic main liquor and are found also in the scrubber liquor.

The total quantity of ammonia is, in fact, insufficient to remove completely the carbon dioxide, hydrogen sulphide and hydrogen cyanide present, and the residuum of the two last has to be removed from the gas later by special purification methods.

Other ammonium salts are formed by secondary reactions. Ammonium sulphide is oxidised by the oxygen present in the crude gas, and later by the oxygen of the air to which it is exposed during storage, giving progressively polysulphides, thiosulphate, sulphite and sulphate. Sulphite is usually present only in faint traces. The cyanide reacts with the polysulphide forming thiocyanate, so that polysulphides are rarely found in the liquor. Cyanide is usually found only in small quantities and is frequently absent altogether (*v. infra*). Small quantities of ferrocyanide are also sometimes formed by the action of the cyanide on the ironwork of the plant, but this is of rare occurrence. In addition to ammonium salts the liquor also contains small quantities of pyridine bases and considerable amounts of substances derived from tar, especially phenols. According to Skirrow (J.S.C.I. 1908, **27**, 58) the phenols in gasworks liquor vary between 0·1 and 0·35 g./100 c.c.

It is convenient to distinguish between the “ free ” ammonia and “ fixed ” ammonia present. The former represents the ammonia present as sulphides, carbonates and cyanide, and in combination with the phenols, all of which are compounds decomposed by heating, and from which the ammonia can be completely recovered by boiling the solution. The latter, the “ fixed ” ammonia, is present as chloride, sulphate, thiosulphate, sulphite, thiocyanate, etc., compounds which are not appreciably decomposed on boiling. For the recovery of the “ fixed ” ammonia it is necessary to add to the liquor a sufficient amount of a non-volatile alkali such as lime or caustic soda, to displace the ammonia. The “ fixed ” ammonia in the final mixture of gas liquor obtained in the storage well is usually from 20 to 25% of the whole, but the proportion of “ fixed ” to total ammonia is higher in the hydraulic main and condenser liquor.

The table at the top of p. 344 gives the results of a number of analyses of ammoniacal liquor from gasworks and coke ovens made by Linder on behalf of the Chief Alkali Inspector, and published in the Annual Reports of the latter. In addition two analyses of German gasworks liquor by Meyer and Hempel (J. Gasbeleucht. 1908, **51**, 428) are given. Both these authorities should be consulted for methods of analysis (Linder, Alkali Inspector's Report, 1909, 15, and Meyer and Hempel, *l.c.*). In these analyses the whole of the carbon dioxide and hydrogen sulphide present are calculated as the normal carbonate and sulphide respectively, and in Linder's analyses the difference between the total sulphur and that present as sulphide, sulphate and thiocyanate is calculated as ammonium thiosulphate.

The existence of free ammonia (*i.e.* dissolved NH_3) or its hydroxide in solution has been disputed. In many cases the acids present are sufficient theoretically to fix all the ammonia present, although the partial dissociation of certain of the salts may still permit the existence of some ammonia in solution as such ; but in hydraulic main liquor there are not infrequently insufficient acidic constituents present to account for all the ammonia, and in these circumstances it would certainly appear that free ammonia must be present. The existence of free ammonium cyanide in the liquor has also frequently been denied, but more perfect methods of analysis have shown that it is undoubtedly often present in small quantity. The amount depends considerably on the time for which the liquor has been stored, *i.e.* on the extent to which secondary reactions in which cyanide is converted to thiocyanate have proceeded.

In gasworks, where the liquor may be stored for some time, the cyanide content is small and sometimes negligible, but in coke-oven liquor, which is usually only stored for a short time before working-up, the cyanide content may be considerable. The presence of cyanide is objectionable, as it increases the amount of HCN in the waste gases from the manufacture of ammonium sulphate. The effect of storing is readily seen from the following analyses given

COMPOSITION OF REPRESENTATIVE GAS LIQUORS.

(All concentrations given as g. per 100 c.c.)

	Gasworks.					Coke ovens.
	Hydraulic main liquor.		Condenser liquor.	Liquor from storage well.		Average of nine samples of liquor.
	English works.	German works.	English works.	English works (av. of 5 samples).	German works.	
Free ammonia	0·721	0·291	3·247	1·929	1·406	0·841
Fixed ammonia	0·306	0·288	0·221	0·613	0·309	0·102
Total ammonia	1·027	0·579	3·468	2·542	1·715	0·943
Ammonium sulphide, $(NH_4)_2S$	0·276	0·073	0·768	0·862	0·276	0·466
Ammonium carbonate, $(NH_4)_2CO_3$	1·320	0·475	8·810	5·000	3·526	1·960
Ammonium chloride, NH_4Cl	0·838	0·722	0·459	1·120	0·738	0·217
Ammonium sulphate, $(NH_4)_2SO_4$	?	0·023	?	0·202	0·023	0·032
Ammonium thiosulphate, $(NH_4)_2S_2O_3$	?	0·143	?	0·173	0·123	0·041
Ammonium thiocyanate, NH_4CNS	0·047	0·100	0·070	0·528	0·182	0·043
Ammonium cyanide, NH_4CN	0·034	0·003	0·070	0·036	0·003	0·070
Ammonium ferrocyanide, $(NH_4)_4FeC_6N_6$	0·019	0·019	0·030	0·038	0·088	nil
Authority	Linder	Meyer and Hempel	Linder	Linder	Meyer and Hempel	Linder

by Linder in the above-mentioned Alkali Inspector's Reports :

	g./100 c.c.	
	Fresh liquor.	Liquor stored for 6 months.
Free ammonia	2·176	1·920
Fixed ammonia	0·576	1·060
Total ammonia	2·752	2·980
CO_2	2·551	2·122
H_2S	0·661	0·205
HCN	0·068	0·000
HSCN	0·369	0·974
$H_2S_2O_3$	0·047	0·266
H_2SO_4	0·018	0·126
Total S	0·855	0·912

Valuation of Ammonia Liquor.—Many gasworks in this country still express the ammonia content of the liquor in terms of "ounce-strength," which originally implied the number of ounces avoirdupois of pure sulphuric acid required to neutralise the ammonia contained in one gallon of the gas liquor. For statistical purposes or for sale the volumes of liquor are frequently converted into the equivalent volume of liquor of 10-oz. strength. The unit of ounce-strength was originally based on the Wills saturation test, but as this took no account of the fixed ammonia, it is now usual to use one or other of two methods to arrive at the total ammonia content. At some works the free and fixed ammonia are distilled off into acid which, at 15°C., contains 10 parts by weight of pure sulphuric acid in 100 parts by volume, titrating from a burette of 1-oz. capacity, graduated in $\frac{1}{8}$ths of an ounce, and subdivided into tenths (*i.e.* into $\frac{1}{80}$ths in all) and to read off the ounce-strength direct. In other cases, $N/1$ sulphuric acid is used, the ammonia content expressed in terms of percentage of ammonia (g. per 100 c.c.), and a factor used for conversion to ounce-strength. The liquor must not be distilled to dryness, as otherwise the thiocyanates may be decomposed with the formation of ammonia, giving high results. To convert g. per 100 c.c. to ounce-strength, the former should be multiplied by 4·61 ; to convert figures in ounce-strength to g. per 100 c.c., the former should be multiplied by 0·217.

For approximate purposes the ammonia content of the liquor is frequently estimated from the specific gravity, 1° Twaddell being usually regarded as equal to 2-oz. strength. While sufficient for such purposes as the control of the day to day working of the washers and scrubbers on the works, such a measurement is quite unsuitable for purposes where fair accuracy is required, as a liquor showing 5° Tw., for example, may vary in actual content from 8- to 12-oz. strength, as against the supposed 10-oz.

In London and the South of England liquor is still sold by, or expressed in terms of, " butts " of 108 gallons.

Distillation of Ammoniacal Liquor.—Ammonium sulphate was made from gas liquor in the very early days of the gas industry by simply neutralising it with sulphuric acid, the solution being then evaporated to give the sulphate. The products so obtained were very impure, containing tarry matter, thiocyanate, etc., and the escaping gases, especially sulphuretted hydrogen, created a nuisance. Nowadays ammonia is invariably recovered from the ammoniacal liquor in the first place by distillation, then adding lime to displace the fixed ammonia. Lime is almost invariably employed for this purpose ; caustic soda has the advantage that it entails less cleaning of the stills, but the cost of the caustic soda is usually prohibitive.

At one time an intermittent process was used, employing externally-fired pot stills, but the use of continuous column stills is now almost universal, except for very small works. The intermittent still is generally less expensive in first cost, particularly for small installations, and is simpler to operate, but the continuous still possesses much greater advantages in that it permits of a reduced fuel consumption, continuous heat interchange, regularity of operation and relatively high output.

The earliest move towards continuous ammonia distillation was made in 1841 by Newton, who at that time adapted the Coffey still for the distillation of gas liquor, but the present type of column still originated with Savalle, who applied his experience in the rectification of alcohol to the problem of gas liquor. Three methods of heating the stills have been used, (1) external firing, (2) heating by means of closed steam coils, (3) heating by live steam. The first method is wasteful in fuel, and gives rise to trouble from lime deposits on the heated portions of the still ; of the other two methods the use of live steam is the most economical and is now almost invariably employed. Dr. Tidy has demonstrated the relative advantages of the three methods on a manufacturing scale ; in dealing with 7,000 gallons of liquor, external heating took 22 hours and gave a 90% efficiency in the expulsion of ammonia ; closed steam coils took 18 hours and gave a 92% efficiency; while live steam (wet) took 14 hours and gave 98·5% efficiency (Parrish's "Design and Working of Ammonia Stills," Benn, 1924).

There are available on the market a considerable variety of ammonia stills which, although differing from one another considerably in details, follow, nevertheless, the same general principles. The principles are best explained by reference to Feldmann's still (B.P. 3643, 1882 ; G.P. 21708), which was introduced as early as 1882 and has been widely applied. It is reasonably representative of modern practice, apart from the design of the plates in the fractionating columns, which has been considerably improved in more modern designs.

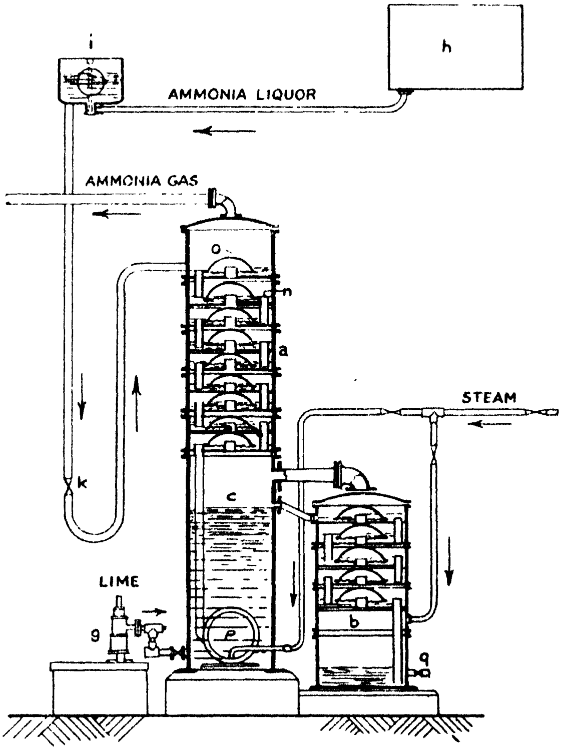


FIG. 8.

In the Feldmann still (Fig. 8) the gas liquor, after being preheated in the economiser (not shown), enters the rectifying column *a*, where it is stripped of the "free" or "volatile" ammonia as it flows downwards in countercurrent with the hot gases rising from the bottom of the still. The column is divided into a number of plates ; the liquor flows across each plate and overflows to the next, the height of the overflow pipe *n* being arranged so that a definite level of liquor is maintained on each plate. The hot gases rising upwards through the central pipe on each plate are brought into intimate contact with the liquor by being forced under the edges of a hood *o*, which surmounts each central pipe and the edges of which, immersed in the liquor, are serrated. From the bottom of the rectifying column *p* the liquor enters the liming chamber *c*, into which milk of lime is pumped continuously or at regular intervals by *g*, whilst the whole is kept agitated by steam injected into the mixture. The liquor enters the liming chamber almost at the bottom, and then flows upwards, being thus mixed with the lime. A sieve is fitted across the chamber, about two-thirds of the way up, to impede the movement of the liquor in this part and to enable clear liquor, fairly free from surplus lime, to flow over to the second column *b* (similar in arrangement to *a*), where the ammonia set free by the lime is driven off. Live steam blown in at the bottom of column *b* provides the heat for distillation and maintains the bottom of the still at such a temperature that all ammonia is expelled. The spent liquor runs away continuously through *q*, and the hot gases pass over to the first column *a*, where they liberate the "free" ammonia and are themselves partly freed from water. *a* and *b* thus perform as a single fractionating column, with lime treatment at an intermediate stage. The hot gases, containing ammonia and a limited quantity of steam, depending on the efficiency and operation of the still, then pass into sulphuric acid in a "saturator," if sulphate is to be made. (The operation of the still is somewhat different if ammonia liquor is to be made—*v. infra.*) The hot gases leaving the saturator pass through the economiser, and thus serve to preheat the liquor, while being themselves cooled and partly condensed.

The "colonne inobstruable," devised by Mallet in 1884, employs a continuous lime feed to a vessel below the first column, with a second column for distilling off the "fixed" ammonia, in which the lime is kept in suspension by rabbles operated from a central rotating shaft.

In other types of still a single column only is employed, the lime being introduced into one of the compartments of the lower portion of the still, which may be made of larger size for this purpose, the hood being also more deeply sealed to effect more vigorous agitation. The mixture of liquor and lime then passes through the lower plates of the still, constructed in a similar manner to those above. A still of this type, manufactured by Bamag (Berlin-Anhaltische Maschinenbau A.-G.), is shown in Fig. 9.

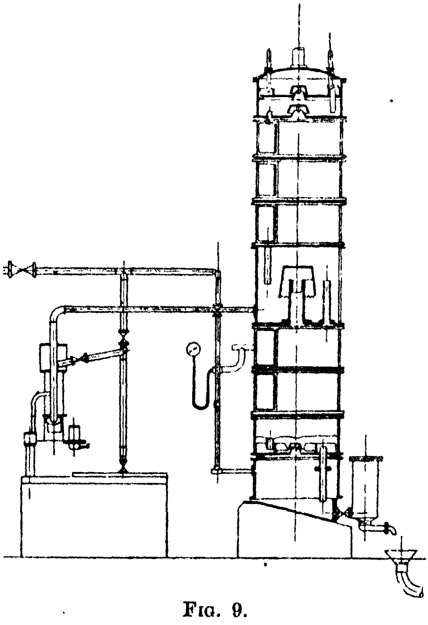


FIG. 9.

More recent improvements have also been made in mechanical details such as the plates and bubble-caps of the fractionating columns, and in making the parts more accessible for cleaning, particularly in those parts of the still where lime is present. Such developments have much in common with the development of general distillation and refinery practice. Wilton (Eng. Pat. 24832, 1901) replaces the circular hood and central pipe (or "upcomer") by an elongated hood with serrated edges placed in the centre of the tray and extending over nearly the full diameter of the still, the rising pipe being then a narrow slot beneath the hood. The hood can be readily removed for cleaning through a manhole at the side.

A fuller development of this type is seen in the Holmes still (Fig. 10), in which for a large still of 5 ft. diameter four tunnel-shaped bubble-caps are used, with large manholes for easy removal. Many other stills of similar type have been designed; they are more fully described in Parrish's "Design and Working of Ammonia Stills," Benn, 1924.

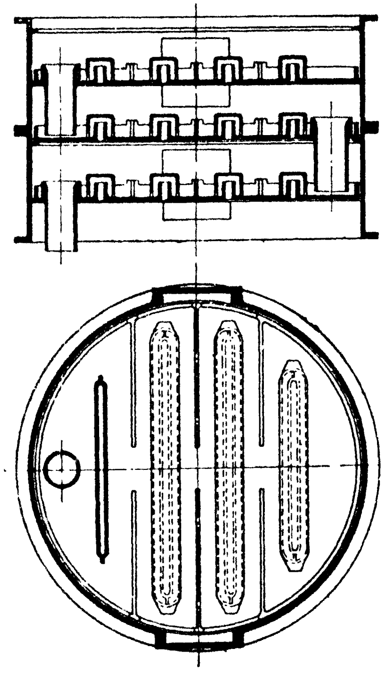


FIG. 10.

A process for distillation of gas liquor under vacuum was patented by Scott (Eng. Pat. 3987, 1900; 11082, 1901), and a number of stills was at one time erected in Scotland. The plant and method of working are described by Ballantyne in J. Gas Light, 1903, **82**, 869. Considerable economy of fuel is claimed, especially where exhaust steam is available, but the validity of these claims is doubtful. Certainly no further development has since taken place in vacuum stills for this purpose.

A novel type of distillation plant has been patented more recently by Holmes, Boocock and Wyld (Eng. Pat. 167719, 1921), in which heated ammonia liquor is sprayed in succession into a number of evaporating chambers. The chambers are heated by jackets in which flue gas circulates.

Absorption of the Ammonia in Sulphuric Acid.—The gases from the still, consisting chiefly of ammonia, steam, carbon dioxide, sulphuretted hydrogen and small quantities of hydrocyanic acid, are conveyed to the saturator, which is charged with sulphuric acid. This is constructed of lead-lined wood or, in more modern saturators, of lead-lined steel. The gases are conducted in by means of a perforated lead pipe, or bell with serrated edges, which serves to distribute them over a large area in the saturator and to keep the liquid thoroughly agitated. The waste gases are conducted away from the upper part of the saturator, and are disposed of by methods described below. The heat of reaction maintains the acid bath at such a temperature (90°–100°C.) that condensation of water is almost entirely prevented, and the ammonium sulphate eventually crystallises out from the acid bath. Steam may be used to assist in keeping the saturator hot, and the vessel may even be insulated.

In the older type of saturator, as shown in Fig. 11, the gases pass in under a bell A, which serves to remove the waste gases, and acid spray is removed by a vessel B, provided with baffles. The sulphate settles on the floor, and is removed by hand, using perforated ladles. The crystals are placed on a lead-lined drain table, fixed so that the mother liquor drains back to the saturator, and are then freed from surplus acid by centrifuging.

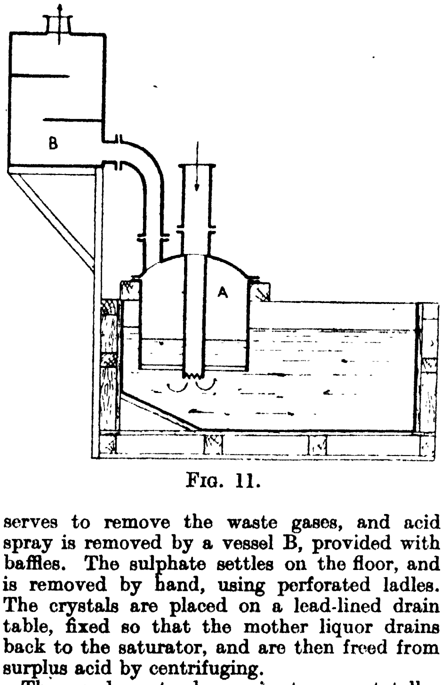


FIG. 11.

The modern tendency is to use totally-enclosed saturators, from which the salt (or rather, mother liquor containing salt) is elevated continuously by means of a steam or air ejector to the drain table, the mother liquor passing back to the saturator and the salt to the centrifuge.

A saturator of this type is shown in Fig. 12. In another closed type, of which the Colson saturator is one of the earliest, salt is removed continuously from the bottom of the vessel, usually cone-shaped, through a special type of valve.

A continuous saturator is normally operated with a bath of low acidity, 3–8% of H_2SO_4 being the normal range, and preferably 5–6%. The acidity is usually very much higher at the outset, when starting a new saturator, being about 25% H_2SO_4, but ammonium bisulphate, NH_4HSO_4, is liable to be formed if the acidity exceeds 10–11% for long. Another reason for maintaining a low acidity is that the presence of a given percentage of mother liquor in the centrifuged salt will entail a lower percentage of acidity than if the bath is strongly acid.

Ammonium Sulphate from Gas Liquor.—Ammonium sulphate made in this way from gas liquor usually contains upwards of 24·5% of ammonia, equivalent to 20·2% of nitrogen, or about 95% of pure ammonium sulphate. It usually contains not more than 0·3% free sulphuric acid, the remainder consisting of moisture and small quantities of insoluble matter. The moisture content of properly dried salt should not exceed 2–3%. The British Sulphate of Ammonia Federation specification for "neutral sulphate of ammonia" is 20·60% nitrogen, not more than 0·025% of free acid, and not more than 0·20% moisture, with a latitude of 0·05%. Most of the sulphate made in the U.K. complies with this specification. Moreover, a considerable proportion of the sulphate made by gasworks, etc., contains at least 21·1% nitrogen. The salt should be pure white in colour, but a greyish colour is sometimes produced by the presence of traces of tarry matter, and discoloration may occur as a result of iron salts building up in the saturator ; this is avoided if the latter is cleaned out from time to time. When sulphuric acid made from pyrites is employed, the resulting sulphate may

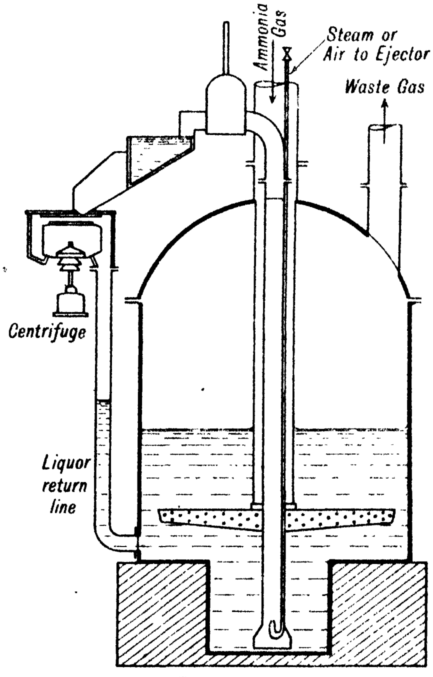


FIG. 12.

be coloured yellow or brown due to the presence of arsenic sulphide. For this reason many manufacturers prefer to use acid made from pure sulphur or from spent oxide. In many cases, however, pyrites acid is used and the arsenic sulphide which rises as a scum to the surface of the liquid (particularly on the addition of oil or tar) is removed as it forms ; preferably, the acid is previously treated with a portion of the waste gases from the saturator and the arsenic precipitated as sulphide by the sulphuretted hydrogen present in these gases. The precipitate is then removed before the acid enters the saturator.

In some cases the sulphate assumes a blue colour on standing in air, owing to the formation of traces of Prussian blue. From the researches of Forbes, Carpenter and Linder (Chief Alkali Inspector's Reports, 1905, 51 ; 1906, 30) it appears that the colour is due to the formation of ammonium ferrous ferrocyanide precipitated with the salt, which is oxidised in the air to form Prussian blue. Apparently, if local alkalinity occurs at some point in the saturator, particularly near the inlet vapours pipe, ammonium ferrocyanide tends to be formed (particularly in the cold) from ammonium cyanide and the traces of iron normally present. The ammonium ferrocyanide, which once formed is quite stable, then reacts with ferrous salts in acid solution to give a white precipitate of ammonium ferrous ferrocyanide, insoluble in acid :

$$FeS+6NH_4CN=(NH_4)_4Fe(CN)_6+(NH_4)_2S$$

$$(NH_4)_4Fe(CN)_6+FeSO_4=(NH_4)_2Fe[Fe(CN)_6]+(NH_4)_2SO_4$$

This is not at first noticed in the salt, but after standing in the air it oxidises to Prussian blue. Priming of the still, leading to the introduction to the saturator of ferrocyanides and thiocyanates in the gas liquor, has a similar effect, but the production of blue salt often occurs in the absence of priming. Its formation is best avoided by maintaining the saturator liquid hot and of sufficient acidity, and by ensuring that the passage of gas shall effect a thorough mixing of the liquid in the saturator, so avoiding the occurrence of local alkalinity.

Waste Products in Sulphate Manufacture.—The waste products from the process are threefold : (*a*) the effluent liquor from the still, (*b*) the aqueous condensate from the cooling of the waste gases in the liquor preheater and from subsequent complete condensation, (*c*) the waste gases themselves.

The effluent liquor is run into settling tanks, where it deposits suspended calcium salts, or "lime sludge," and is allowed to cool. The sludge contains calcium sulphate, carbonate, hydroxide and sulphide, together with some 60% of water, and is usually dumped in pits and covered up with soil.

Disposal of the clarified effluent is frequently troublesome. It contains calcium thiosulphate and thiocyanate, together with phenols and some tarry matter and, although, by arrangement with the local authorities, it is in some plants turned to the sewers or even, with sufficient dilution, discharged into a river, this practice is frequently not permitted without some preliminary purification. It is sometimes got rid of by using it to quench the hot coke from the retorts, and in some cases is even evaporated to dryness, although the latter method is obviously expensive. A more elaborate method is oxidation of the impurities by bacterial treatment. The liquor, preferably circulated as a dilute solution, is passed through coke filters inoculated with sewage bacteria, which oxidise the thiocyanate and also destroy the phenols. The purified effluent may then be discharged into rivers. The blowing of hot flue gas through the effluent liquor also decolorises it and removes some of the phenols ; a Koppers process for the recovery of phenols operating on this principle, in which the phenols are removed from the hot ammonia liquor between the free and fixed ammonia still and absorbed in caustic soda, has been adopted with success at a number of American coke-oven plants.

One of the claims of the direct method of sulphate production described below, in which the gases are received direct in sulphuric acid and are not condensed and redistilled as in the normal gasworks process, is that the formation of a troublesome effluent is avoided.

On the subject of effluent disposal in general, the Reports of the Liquor Effluents and Ammonia Committee of the Institution of Gas Engineers should be consulted (Nos. 1–5, 1931–1935).

The aqueous distillate obtained by cooling the waste gases is a very evil-smelling liquid, and very poisonous, since it contains CO_2, H_2S, and HCN. It is known as "devil liquor" and is difficult to dispose of. Failing any other means of disposal, it is usual to mix the devil liquor with the crude gas liquor going to the still, thus increasing the bulk of the liquor to be distilled.

The waste gases, after cooling and condensation of the devil liquor, consist chiefly of CO_2, with 13–20% of H_2S and smaller quantities of HCN, as well as strongly smelling empyreumatic vapours derived from the tar. They cannot be discharged with impunity into the atmosphere. With coke-oven liquors, which often contain considerable quantities of cyanide, the amount of HCN may be considerable, and additional care is necessary when dealing with the waste gases. One method of disposing of the gases is to burn them under the boilers, retorts, or other furnaces, the products of combustion being discharged by the chimney stack ; where there is an adjacent sulphuric acid plant, as in many large works, the gases are burnt in the sulphur, pyrites, or spent oxide burners and are used as a source of SO_2. With small and medium-sized works, the H_2S and HCN are removed by iron oxide, in a similar manner to that employed for the dry purification of coal gas. In place of purifying boxes conical heaps of oxide on a concrete floor are often used, the gas being introduced from the bottom at the centre of the heap. The spent oxide is, of course, used for sulphuric acid manufacture.

A considerable proportion of waste gas is converted into sulphur by burning in Claus kilns, a process similar to that used for sulphur recovery from Leblanc alkali waste (Eng. Pat. 3606, 1882 ; 5070, 1883 ; 5958, 1883). By this method sufficient air is mixed with the gas to react with the H_2S in accordance with the equation $2H_2S+O_2=2H_2O+2S$, and the mixture passed through a kiln containing a bed of ferric oxide, which is kept hot by the combustion. The sulphur formed is deposited in cooling chambers and the residual gases passed through a small tower packed with wetted limestone to remove traces of SO_2, and finally through an iron oxide purifier to remove any residual H_2S. The sulphur obtained is not very pure, owing to tarry material, etc., present in the gas.

Recovery of Ammonia as Liquor.—The ammonia from coal distillation is also recovered and marketed as a solution in water.

A crude aqueous solution of ammonia, containing sulphide and sometimes carbonate, is manufactured in considerable quantities for use in the ammonia-soda process and for the production of other ammonium salts. This crude product is termed *concentrated gas liquor*. It contains 15–18% total ammonia, with relatively large quantities of sulphide and carbonate present.

In the manufacture of this liquor, the gases passing over from the top of the ammonia still (the gases which in sulphate manufacture pass to the saturator) are simply condensed in a direct condenser, and the gases leaving the condenser are scrubbed with water. To obtain a sufficient concentration of ammonia a reflux condenser is attached to the top of the still so that, as in normal still practice, the ratio of ammonia gas to water vapour leaving the top of the still may be reduced as desired by increasing the amount of liquor which falls from plate to plate in the fractionating column. It is not possible, working in this manner, to obtain concentrations of ammonia above 15–18% ; at higher concentrations solid ammonium carbonate and carbamate separate out in the condenser and cause blockages.

A more concentrated solution is marketed as *concentrated ammonia liquor*, containing about 25% of ammonia, a small amount of sulphide and little or no carbonate. In preparing concentrated ammonia liquor, the crude gas liquor is first heated to a temperature rather below 100°C. in a "dissociator" or "decomposer," at which temperature a large proportion of the CO_2 and H_2S is driven off, accompanied by only small quantities of ammonia. The dissociator is designed with plates, like a still, and is heated with both direct and indirect steam. The ammonia lost at the top of the dissociator is removed by washing the evolved gases with water, the solution thus obtained being sent to the still.

As Parrish points out in his "Design and Working of Ammonia Stills," the loss of ammonia from the dissociator need only be small if this portion of the plant is properly designed ; the ammonia expelled in the lower portion of the dissociator is largely reabsorbed by the cooler liquid higher up. This author also emphasises the advantages to be gained by the use of a pressure dissociators gauge, working at, say, 20–50 lb. per square inch, since the dissociation of the carbonate and sulphide is not materially affected, while the strength of ammonia solution in equilibrium at the higher pressure is greater.

The decomposed gas liquor is then distilled as in sulphate manufacture, with the addition of sufficient lime to liberate the fixed ammonia. The still is fitted with a reflux condenser or dephlegmator, by means of which a sufficient reflux is maintained in the fractionating column so that the vapours passing over to the final condenser will not contain more than the ratio of steam to ammonia necessary to give a 25% solution on condensation. In certain plants the vapours from the reflux condenser are washed with milk of lime before passing to the final condenser, in order that further quantities of H_2S and CO_2 may be removed. The milk of lime is then used in the fixed ammonia still to avoid loss of lime or dissolved ammonia. The lime washing process can be eliminated by the use of a pressure dissociator, referred to above, which will permit of a sharper separation between ammonia and the other gases. Concentrated ammonia liquor is usually of a yellowish colour ; it contains about 25% NH_3, with not more than 0·5% H_2S. It is usually almost free from carbonate. Small amounts of cyanogen compounds, derived from the HCN evolved from the crude liquor, are usually present as cyanide, ferrocyanide, and thiocyanate, although the cyanide tends to disappear fairly rapidly and ferrocyanide is frequently absent. For the manufacture of ammonium nitrate, by way of the ammonia oxidation process, such cyanogen compounds should not exceed 0·01 g. per 100 c.c. (expressed as ammonium thiocyanate). In addition small amounts of phenols and pyridine bases are always present.

A much purer form of ammonia solution is manufactured as *liquor ammonia*, or "pure caustic ammonia." The method of production is similar to that for concentrated ammonia liquor as given above, except that the final still is operated with a higher reflux so that the vapours issuing from the dephlegmator or reflux condenser are practically free from steam and consist of ammonia gas only. The last traces of H_2S, CO_2, or HCN are commonly removed by scrubbing in a number of towers with milk of lime, as cited above, ferrous sulphate being sometimes added to the last lime washer to assist in H_2S removal. The ferrous hydroxide formed retains the H_2S as ferrous sulphide. Pfeiffer (J. Gasbeleucht. 1900, **43**, 89 ; 1903, **46**, 1 ; J.S.C.I. 1903, **22**, 142) recommends the use of a final caustic soda washer containing 10% caustic soda solution to absorb accidental traces of H_2S. Foucar recommends the use of ammonium persulphate or sodium permanganate. The gases then pass through a number of absorbers containing wood charcoal, which remove the strongly-smelling empyreumatic substances derived from the tar. Additional purification may be obtained by passing the gas through a fatty or high-boiling mineral oil. The resulting pure gas is then led into distilled water, and a solution made of any strength up to about

35%. Spare charcoal scrubbers are usually provided so that the charcoal, which loses its activity after a time, can be steamed to recover ammonia and then revivified by heating in closed retorts.

Pure liquor ammonia should be clear and colourless, even after exposure to light for some time. It should be practically free from empyreumatic matter and from pyridine, and should be free from sulphides as shown by the lead acetate test. Its strength is usually ascertained from its specific gravity.

Anhydrous liquid ammonia is also made from gas liquor in the same manner as that described above for pure liquor ammonia, but instead of passing the gas into water it is dried (by passing through towers filled with lime or caustic soda, or by refrigerating the gas so that the bulk of the water is deposited), sometimes treated with oil to remove pyridine, etc., then compressed in an ammonia compressor and the gas condensed by cooling.

Direct and Semi-Direct Processes for Ammonia Recovery.—As outlined above (*cf.* Fig. 7), the direct process consists in the absorption of the hot gas direct in sulphuric acid, and the semi-direct process in the removal of the tar and virgin liquor by cooling in the normal way, after which the gas is passed into sulphuric acid instead of being scrubbed with water as in the indirect process. The incentive to perfect the direct and semi-direct processes has been considerable, in view of the obvious savings in evaporation of water, apart from the greater simplicity of plant.

The first attempt at direct recovery was made by Brunck, who passed the hot gases containing tar direct into sulphuric acid. The sulphate so made was badly contaminated and unsaleable. Brunck improved the method considerably with a tar extractor, and the process has since been developed by Otto & Co. as the Otto-Hilgenstock Direct Recovery process (Hilgenstock, Stahl u. Eisen, 1909, 1644). The hot raw gases are freed from tar by scrubbing with a tar spray, so that the temperature of the tar does not rise above 70°–80°C. The gas leaving the spray contains not more than 4 grains per 100 cu. ft. of tar and then passes direct to a saturator, the sulphate produced from which is said to be pure white. The separation of tar above the dew-point of the gas is a difficulty, since this means in turn that the saturator must be maintained at a high temperature (110°C.) to avoid condensation of water.

The direct recovery process is in operation at a number of coke ovens in Europe, but its difficulties have led to the introduction of the semi-direct process, outlined above. Another disadvantage of the direct process which should be mentioned here is that it is quite inflexible; unlike the indirect process, which permits of the manufacture of ammonia or ammonium salts in any form, the direct process can only recover ammonia as sulphate.

The semi-direct process was devised and developed by Heinrich Koppers (G.P. 184846, 224846). In it the gas is cooled in the usual indirect coolers well below dew-point; the virgin liquor which is condensed is distilled in the usual way and the ammonia gas which results from the distillation joins the main stream of gas before the saturator. The whole is preheated to 40°–60°C. by the hot raw gas before passing to the saturator. A semi-direct process, differing in certain particulars from that of Koppers, has been developed by Otto.

According to Gluud (Chem.-Ztg. 1922, **46**, 716) the relative costs of making sulphate by the direct, semi-direct, and indirect methods are as 1 : 1·1 : 1·3. This comparison probably favours unduly the direct process.

TECHNICAL FORMS OF AMMONIA.

Ammonia is sold from gasworks or coke ovens as a solution in water in at least three forms—concentrated gas liquor, "concentrated ammonia liquor," and "liquor ammonia" (pure ammonia solution). These forms are described above under "Recovery of Ammonia as Liquor." The ammonia obtained by the synthetic process is very much freer from impurities, and a relatively pure solution is made direct by passing the gas obtained by releasing the product from the pressure receivers into water. For the purest product, filtration from traces of oil and the use of distilled water are necessary. In synthetic plants, such as the Haber-Bosch, where the ammonia is removed by water scrubbing, the solution so made is used without further treatment for sulphate manufacture, etc. It is sometimes contaminated by traces of oil, which, however, are not sufficient to affect the subsequent process. Ammonia liquor is transported in carboys, steel drums and steel tank wagons; for the purer product the drums or wagons are tinned, cement-washed or glass-lined, to avoid contamination with iron and discoloration due to precipitates of iron oxide.

Ammonia is also marketed as the anhydrous liquid in this country in cylinders, principally for use in refrigeration. In the U.S.A. transport of anhydrous ammonia in steel tank wagons holding up to 50,000 lb. is standard practice, a large proportion of the ammonia so transported being used for the ammoniation of superphosphate (*see* "Ammonium Phosphate" *below*).

AMMONIUM SALTS.

Ammonium Sulphate, $(NH_4)_2SO_4$, is the most important ammonium salt industrially, the world's annual production exceeding three million tons. Of this, about 38% is made in gasworks, coke ovens and the like, and 62% from synthetic ammonia (1934–35).

The manufacture of by-product ammonium sulphate has already been described. In a number of synthetic ammonia works the process of sulphate manufacture follows very similar lines: ammonia gas obtained on releasing the pressure from the ammonia solution or anhydrous liquid collected in the high-pressure receivers is absorbed in sulphuric acid in saturators and is crystallised therefrom. In the larger synthetic ammonia works, however, such as those of the I.G. in Germany, of the I.C.I. in England, and of the French State Works at Toulouse, calcium sulphate (as gypsum or anhydrite) is used in place of sulphuric acid, as a cheaper source of the sulphate radicle. The reaction follows the equation :

$$2NH_3+CO_2+H_2O+CaSO_4 = CaCO_3+(NH_4)_2SO_4$$

In the method of hydrogen manufacture which is employed in these factories, namely, the catalytic water-gas process, large volumes of carbon dioxide (roughly 1 mol. of CO_2 per mol. of NH_3) are removed from the catalysed water-gas by scrubbing with water. The major part of this CO_2, more than sufficient for the purpose, is available for the sulphate process. Ammonia liquor from the synthesis plant, diluted to about 15% NH_3, is carbonated by passing it down towers in counter-current with CO_2 gas, adequate provision being made for cooling the liquor. The finally carbonated liquor contains CO_2 and NH_3 in roughly stoichiometric proportions. Finely ground anhydrite or gypsum is then added in such quantity that there is an excess of ammonium carbonate, and kept in suspension by stirring at a temperature of about 70°C. The reaction, which is usually carried out continuously in a number of large reaction vessels in series, with cascade flow from one vessel to the next, is complete in 6 to 9 hours. In some plants the CO_2 and NH_3 are passed direct into the reaction vessels, which contain a suspension of calcium sulphate in water. The excess of NH_3 and CO_2 is driven off by heating the liquor after the precipitated calcium carbonate has been filtered off, and the solution, containing at this stage about 55 g. per 100 c.c. of ammonium sulphate, is evaporated in vacuo and crystallised. The crystals are centrifuged and finally dried by hot air in rotary driers (F.P. 427065, 1910 ; G.P. 281174, 1913 ; 300724, 1916 ; 336767, 1917 ; 382004, 1921). A more recent development which has been applied on the large scale in a number of synthetic ammonia works is the Fauser process, in which sulphuric acid is sprayed into chambers in counter-current with ammonia gas : the heat of reaction is sufficient to produce solid sulphate, which is removed from the bottom of the chamber. The granular material appears to be practically non-caking (Fauser, Chem. Met. Eng. 1931, **38**, 456).

Synthetic ammonium sulphate generally contains about 21·1% nitrogen (99·5% pure approx.) and is neutral. The moisture content is less than 0·2%. When stored for some time, ammonium sulphate has a tendency to cake, this tendency depending on a number of factors. Considerable attention has been paid in recent years to the production of free-flowing crystals of ammonium sulphate, in order that the product may be more easily handled in storage and by the farmer. In the Dutch synthetic ammonia plants at Lutterade and Ijmuiden phosphates or phosphoric acid are added to the saturator to induce the formation of large crystals (Z. Kunstdünger-Ind. 1935, p. 149).

According to B.P. 330947 and 330945 (Adams) the crystal shape of ammonium sulphate can be altered from approximately equi-dimensional to rice-shaped crystals by effecting the crystallisation in an acid solution containing a trace of a trivalent ion. Crystals of rice-shape are found to be particularly free from caking. The effect of impurities on the crystal size of ammonium sulphate is also discussed by Berkhoff (Chem. Trade J. 1935, **96**, 417, and Chem. Weekblad, 1935, **32**, 186) and by Gluud and others (Ber. Ges. Kohlentech. 1931, **3**, 371).

Ammonium Carbonate (Sal-volatile).—The commercial product sold under this name is actually a double salt of ammonium bicarbonate and carbamate, corresponding with the formula $NH_4{\cdot}HCO_3,NH_2{\cdot}CO{\cdot}ONH_4$ and contains usually about 31% of ammonia and 56% of carbon dioxide. It was formerly made by heating a mixture of about 1 part of ammonium sulphate with 1·5 to 2·0 parts of chalk in iron retorts, the evolved gases being passed into water-cooled leaden chambers, where the carbonate was deposited as crusts on the walls. The crust was detached when sufficiently thick and usually resublimed for purification.

It is now more usual, in synthetic ammonia plants in which CO_2 is available as a waste product, to pass CO_2 and NH_3 gas with steam into lead chambers as above, or direct into water, the particular compound separating out under suitable conditions of temperature of precipitation and the ratio of NH_3 to CO_2 used.

The commercial product forms crystalline crusts, smelling strongly of ammonia, which is partly evolved on exposure to air, leaving a powder consisting of ammonium bicarbonate. It is used in the manufacture of baking powders and smelling salts and in dyeing and wool-scouring.

Ammonium Bicarbonate, $NH_4{\cdot}HCO_3$, is also manufactured as an alternative to sodium bicarbonate for use in baking powder, and for neutralising acid ammonium sulphate. It is made by passing CO_2 and steam into ammonium carbonate solution, or by direct synthesis from NH_3 and CO_2 gas, these being passed into solution in stoichiometric proportions at about 40°C. Bicarbonate separates out and is centrifuged and dried.

Ammonium Chloride, NH_4Cl (Sal-ammoniac).—The manufacture of this salt in gasworks and coke ovens using a method similar to that employed for the sulphate (namely, passing the gases from the stills into hydrochloric acid) has been practised, but lead is attacked under these conditions and the saturator must be constructed of stoneware or similar material, which has obvious disadvantages. It is usually made in such works by neutralising hydrochloric acid with concentrated gas liquor, and evaporating and crystallising the resulting solution. Ammonium chloride can also be made from the sulphate by evaporating a solution of ammonium sulphate and sodium chloride in equivalent proportions : the sodium sulphate formed separates out as the monohydrated salt and is removed, leaving finally a concentrated solution of ammonium chloride which is crystallised. Freeth and Cocksedge (B.P. 26263, 1909 ; F.P. 414682 ; U.S.P. 970909) mix equivalent quantities of ammonium sulphate and sodium chloride at about 103°C. with enough water to obtain a saturated solution of ammonium chloride and sodium sulphate; ammonium chloride is then crystallised out by cooling down to 30°C.

It is also manufactured by the action of ammonium carbonate (or ammonia and carbon dioxide) on calcium chloride solution, which is obtained in large quantities as a by-product in the ammonia-soda process. The solution of ammonium chloride obtained is evaporated and crystallised after filtering off the precipitated chalk (U.S.P. 805581).

Claude proposed to manufacture ammonium chloride by a modification of the ammonia-soda process, similar to the calcium sulphate process for ammonium sulphate, using the reaction ·

$$NaCl+NH_3+CO_2+H_2O=NaHCO_3+NH_4Cl$$

Since the solution of ammonium chloride obtained in this way is saturated with sodium bicarbonate, it is difficult to separate pure ammonium chloride, but a process in which very low temperatures are employed has been applied successfully in a number of soda works. The Ges. für Kohlentechnik has developed a successful process in which the solution is treated alternately with CO_2 and NH_3 and then with sodium chloride (B.P. 130365, 1918 ; 131870, 1919 ; G.P. 349348, 1920, etc.).

A very pure form of the salt, in fibrous crystals similar to those obtained by sublimation, is obtained by mixing dry hydrogen chloride diluted with hydrogen (prepared by combustion of chlorine in excess hydrogen) with almost dry ammonia under such conditions that the temperature of reaction is 230°-310°C. (B.P. 273093, 1926 ; 274263, 1926 ; 290045, 1927). The size of the crystals obtained from aqueous solutions is increased by the addition of an extract of soya bean wax (G.P. 467184, 1926), or of pectin (G.P. 481696). It may be obtained as cubic crystals by adding small quantities of ammonium acetate to the crystallising solution.

Ammonium chloride is frequently purified by sublimation, the sublimed product being known as *sal-ammoniac*. Large externally heated iron pots are used, covered with a concave iron plate on which the salt is sublimed. The salt immediately in contact with the iron is discoloured and is removed prior to sale. The discoloration is avoided by using earthenware pots, which have, however, to be destroyed at each operation.

Ammonium chloride has not found favour as a fertiliser, partly on account of cost and partly because of possible injury to crops arising from the sum-total of the chlorine in the ammonium chloride and the chlorine in other fertiliser constituents such as potassium chloride. Where the total chlorine present has no adverse effect, nitrogen in this form is as effective as in sulphate.

The commercial crystallised salt is white or only slightly discoloured. The sublimed salt has a fibrous structure and frequently contains traces of iron. Ammonium chloride is used in pharmacy, in galvanising, in soldering, for dyeing and calico-printing and for use in electric cells of the Leclanché type.

Ammonium Nitrate, $NH_4{\cdot}NO_3$, is manufactured by oxidising ammonia to nitric acid and then neutralising the resulting acid with a further quantity of ammonia. In the usual method employed, ammonia gas is passed into the solution of 40–50% nitric acid which results from the oxidation process, in vessels which are cooled to prevent excessive temperature rise and consequent loss of nitric acid, which has a lower boiling-point than that of the nitrate solution ; a strong solution is thus made, from which, after further evaporation, crystals of ammonium nitrate are obtained. Crystallising troughs of the Passburg type are commonly employed for the final operation.

In more recent processes for the manufacture of ammonium nitrate, advantage has been taken of the heat of neutralisation and the heat of crystallisation in concentrating the solution. The very successful process developed by Fauser (B.P. 367660) is described in L'Ind. Chimica, 1931, **6**, 870. This process is operated under a pressure of 5 atmospheres absolute so that a high temperature may be maintained in the saturator, facilitating the production of a concentrated solution, while at the same time loss of nitric acid is avoided, since the pressure is higher than the vapour pressure of nitric acid at this temperature. The acid is first freed from dissolved oxides of nitrogen by treatment with air in a quartz-packed tower (to avoid possible detonation of the nitrate), and the preheated, denitrated acid introduced into the pressure saturator (made of special high chromium alloy steel), where it is treated with ammonia gas at 155°–160°C. The hot nitrate solution, discharged into a vessel surrounding the saturator, immediately boils and a 90% ammonium nitrate solution is obtained directly in this way. From this the salt can be crystallised without further evaporation and dried with hot air. A slight excess of ammonia is used in the saturator and the vapour released on boiling, after being used to preheat the nitric acid, is passed through a rectifying column to recover the ammonia as gas. The Fauser process is in operation at the Montecatini plants in Italy (Merano, Bussi, Novare, and Crotone), at the Rouen plant of the S.A. Potasse et Engrais, at the Willebroeck and La Madaleine plants of the S.A. Ammoniaque Syn. et Der., and at the Ljungawerk of the Stockholm Superphosphat.

Ammonium nitrate is used extensively as a fertiliser, and for the manufacture of explosives (*v. infra*) and nitrous oxide. It is hygroscopic and very liable to cake ; for use as a fertiliser it is usually mixed with other materials, which may or may not have any agricultural value, such as ammonium sulphate (*Leunasalpeter*), calcium carbonate (*nitrochalk*, *Cal-nitro*), or clay.

Ammonium Phosphate.—With a few minor exceptions the only salts of phosphoric acid which occur naturally are the orthophosphates ; they are also the only salts of phosphoric acid which are used as fertilisers. Their more important properties are summarised in the following table (Ross, Merz and Jacob, Ind. Eng. Chem. 1929, **21**, 286 ; Warren, J. Amer. Chem. Soc. 1927, **49**, 1904) :

	Crystal form.	Solubility at 25°C. g. per 100 g. water.	Heat of formation from NH_3 gas and solid H_3PO_4 g.-cal./ g. mol.	NH_3 vap. pressure mm. Hg.		p_H of 0 1*N* soln.
				100°C.	125°C.	
Monammonium phosphate, $NH_4 \cdot H_2PO_4$ . .	Tetragonal	41·6	29,000	0·0	0·05	4·4
Diammonium phosphate, $(NH_4)_2HPO_4$.	Monoclinic	72·1	48,500	5·0	30·0	7·8
Triammonium phosphate, $(NH_4)_3PO_4,3H_2O$	Ortho-rhombic	24·2	58,400	643·0	1,177·0	9·0

The solubilities of monammonium phosphate and of ammonium sulphate are about the same at 65°C., while at lower temperatures the sulphate is more soluble and at higher temperatures the phosphate is more soluble.

The processes generally used for the manufacture of the ammonium phosphates involve two stages : the preparation of phosphoric acid and the subsequent neutralisation of the acid by ammonia. Phosphoric acid is almost invariably made from phosphate rock, two methods being employed. One, known as the pyrolytic or volatilisation method, involves the distillation of the rock with silica and carbon at high temperatures ; the other, known as the wet method, consists in the treatment of the rock with sulphuric acid. The acid obtained by the first method is upwards of 75% concentrated, by the second method not more than about 25%. Phosphate rock is a basic phosphate, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, in which part of the hydroxyl group has been replaced by fluorine.

From the acid made by the volatilisation method, the monammonium salt is obtained by adding the acid and ammonia gas, in equivalent quantities, to the mother liquor from a previous batch until the solution is nearly saturated at the temperature to which it is raised by the heat of reaction. The salt is crystallised by cooling, and centrifuged. For the diammonium salt, the acid is used in excess and the temperature is not allowed to exceed 80°–90°C. ; the remainder of the ammonia is added after cooling, until a diluted portion of the solution reacts neutral to cresol red (U.S.P. 1670504, 1928 ; B.P. 256137, 1926). In a modification of this process (Klugh and Seyfried, U.S.P. 1822040, 1931) phosphoric acid is added to the mother liquor and ammonia gas introduced in sufficient quantity to give a ratio of monammonium to diammonium salt of 85 : 15. The heat of neutralisation serves to evaporate water, and the concentrated solution is then saturated with ammonia in a cooled and gas-tight rotary drum until the formation of the diammonium salt is complete. The salt crystallises out in the drum and is filtered off and dried below 80°C.

The preparation of ammonium phosphates from the phosphoric acid made by treating phosphate rock with sulphuric acid is complicated by the fact that on neutralising with ammonia the 25% solution of acid so obtained, a gelatinous precipitate of iron and ammonium phosphates separates out, which is difficult to filter. In the process which is more usually employed a solution of monammonium phosphate in sulphuric acid is made by replacing part of the sulphuric acid used for treating the rock by ammonium sulphate, according to the equation :

$$Ca_3(PO_4)_2 + (NH_4)_2SO_4 + 2H_2SO_4 \\ 3CaSO_4 + 2NH_4 \cdot H_2PO_4$$

The solution so obtained is acid, some excess of sulphuric acid being used, and is filtered free of the calcium sulphate sludge. The clear solution is neutralised with ammonia, the sludge of iron and aluminium phosphates filtered off and the solution evaporated to crystallise out the monammonium phosphate, care being taken to ensure that the concentration of sulphate is kept sufficiently low to avoid crystallisation. The calcium sulphate which separates out earlier in the process can be used to make ammonium sulphate by the method described above.

Ammonium Salts as Fertilisers.—In addition to ammonium nitrate and sulphate, both of which supply nitrogen to the soil in differing concentration, there has been an increasing attention paid to the use of concentrated fertilisers and of complete fertiliser mixtures which supply phosphoric acid and potash in addition to nitrogen. The ammonium phosphates, which supply nitrogen and phosphoric acid simultaneously, have been considerably developed ; typical examples of marketed **N** and PO_4 fertilisers are *Ammophos* (monammonium phosphate with small quantities of sulphate and of iron and aluminium phosphate), *Leunaphos* (a mixture of diammonium phosphate and sulphate), and *ammoniated superphosphate*, obtained by treating superphosphate with ammonia gas. An ammoniating solution containing synthetic urea (made from CO_2 and NH_3) is marketed in the U.S.A., as is also a solution of ammonium nitrate in 50% ammonia liquor.

Complete mixtures, containing **N**, **PO_4**, and **K**, are sold in Germany under the name *Nitrophoska*, and in this country as *Concentrated Complete Fertilisers.*

Bibliography.—Lunge, "Coal Tar and Ammonia," Part III, 5th ed., Gurney and Jackson, 1916; Meade, "Modern Gasworks Practice," Benn, 1921; Gluud and Myers, "International Handbook of the By-Product Coking Industry," Benn, 1932; Rambush, "Modern Gas Producers," Benn, 1923; Parrish, "Design and Working of Ammonia Stills," Benn, 1924; Wigginton, "Coal Carbonisation," Baillière, Tindall and Cox, 1929; Martin, "Industrial Gases," Crosby Lockwood, 1918; Calvert, "Manufacture of Sulphate of Ammonia and Crude Ammonia," Benn, 1917; Muhlert, "Die Industrie der Ammoniak-und-Cyan-Verbindungen," Otto Spamer, 1915; McKee, "Shale Oil," Chemical Catalog Co., 1925; Curtis, "Fixed Nitrogen," Chemical Catalog Co., 1932; Pollitt, "Synthetic Nitrogen Industry," Transactions 2nd World Power Conference, Berlin, **2**, 145, 1930; Waeser, "Atmospheric Nitrogen Industry," Churchill, 1926.

J. R. P.

AMMONIUM NITRATE, AS A CONSTITUENT OF EXPLOSIVES.

Ammonium nitrate occurs in the form of colourless crystals which are deliquescent in moist air and easily soluble in water, the solution being accompanied by considerable absorption of heat. It is used to some extent as a fertiliser, being superior to ammonium sulphate for this purpose on account of the additional nitrogen in the acid radicle. Large quantities are also employed in the manufacture of explosives (*see* EXPLOSIVES).

Ammonium nitrate may be produced by any of the following methods:

(i) direct neutralisation of aqueous ammonia by nitric acid;
(ii) the passage of gaseous ammonia and carbon dioxide through an aqueous solution of calcium nitrate, calcium carbonate being precipitated;
(iii) the passage of nitrous fumes into aqueous calcium cyanamide, giving a mixture of the nitrates of calcium and ammonium;
(iv) the double decomposition of calcium nitrate and ammonium sulphate, calcium sulphate being precipitated;
(v) the double decomposition of sodium nitrate and ammonium sulphate.

Since the introduction of synthetic ammonia and nitric acid as commercial products, a large proportion of the total output of ammonium nitrate has been made by the direct combination of these two ingredients, the resulting material having a purity of about 99·8%.

If gas-works ammonia is used instead of the synthetic material, the product is liable to contain small amounts of pyridine, thiocyanates, and cyanogen compounds of the Prussian blue type. These are often very undesirable when the ammonium nitrate is to be used as an explosive ingredient.

During the war of 1914–18 enormous quantities of ammonium nitrate were produced by method (v) referred to above. This process, patented by Freeth and Cocksedge (B.P. 126678), depends on the difference in the relative solubilities of ammonium nitrate and sodium sulphate in water at different temperatures. Starting with a hot solution saturated with respect to ammonium nitrate, sodium nitrate and sodium sulphate, by suitably manipulating the temperature and concentration, alternate depositions of ammonium nitrate and sodium sulphate are obtained. Further charges of ammonium sulphate and sodium nitrate in equimolecular proportions are added after each cycle of operations. When carefully carried out this process is capable of producing ammonium nitrate of about 99% purity.

Ammonium nitrate exists in at least five crystalline forms, which are named by Greek letters, starting from the form which is stable at the lowest temperature, or by Roman numerals in the reverse order. R. G. Early and T. M. Lowry (J.C.S. 1919, **115**, 1387) record the following transition temperatures. The fused liquid, when perfectly dry, freezes at 169·6°C., forming cubic crystals of ϵ (or I) ammonium nitrate; at 125·2° the salt passes into the δ (or II) form, consisting of rhombohedral crystals which are doubly refracting; a further transition to the γ (or III) variety occurs at 84·2°, the crystals being monoclinic in form and the change being accompanied by an abrupt expansion which may fracture a glass vessel in which a fused sample is cooled; at 32·1° the material passes into the normal rhombic β (or IV) form, this transition being easily observed by the prolonged lag in the temperature gradient when the nitrate is allowed to cool through this point, and a final change to the α (or V) salt occurs at −18°, the crystals being tetragonal and doubly refracting.

The specific heats of three of these forms are given by M. Bellati and R. Romanese (Atti Ist. Veneto 4, 1935), in calories per grm. at atmospheric pressure, as follows: II, 0·426; III, 0·355; and IV, 0·407. The specific gravity of the form stable at ordinary temperatures, *i.e.* the β or IV form, is given by U. Behn (Proc. Roy. Soc. 1907, **80A**, 444) as 1·725 at 20°C. The specific heats of aqueous solutions between 18° to 50°C. are as follows:

% NH_4NO_3	64	47·1	28·6	15·1	9·1
Specific heat	0·6102	0·697	0·7227	0·8797	0·9249

The specific gravity of aqueous solutions at different temperatures (water at 4° is unity) is given by H. Gorke ("Ueber Lösungen stark dissoziierter Elektrolyte," Leipzig, 1905) as follows:

% NH_4NO_3	0°	18°	60°	100°
10·00	1·046	1·0405	1·0231	0·9988
19·77	1·091	1·0835	1·0628	1·0372
40·15	1·186	1·1778	1·1545	1·1258
59·94	1·293	1·2813	1·2546	1·2288

The solubility curve for ammonium nitrate in water exhibits breaks in continuity corresponding with the transition points of the solid. According to published data a saturated solution contains the following percentages of NH_4NO_3: at 0°C., 54·2%; at 20·2°C., 65·8%; at 70°C., 83·3%; at 90°C., 88·1%; and at 100°C., 89·7%.

Solid ammonium nitrate is deliquescent in air in which the vapour pressure of water exceeds 9 mm. at 20°C. (corresponding with the vapour pressure of its saturated solution).

A considerable absorption of heat occurs when ammonium nitrate is dissolved in water, a fall of about 27° being observed when 60 parts of the salt are dissolved in 100 parts of water at ordinary temperature.

A temperature of −32°C. can be obtained by the use of a freezing mixture consisting of ammonium nitrate 5 parts, sodium chloride 5 parts and snow 12 parts.

The heat of solution for 1 mol. in 200 mols. of water is given by J. Thomsen as −6·3 Cals. (J. pr. Chem. 1880 [ii], **21**, 449).

Ammonium nitrate is soluble in absolute ethyl alcohol to the extent of 10% at 80°C., and in absolute methyl alcohol, 40% at 60°C. (A. Fleckenstein, Physikal. Z. 1905, **6**, 419). These solubilities are naturally increased as the alcohol is diluted with water.

Chemical Properties.—In common with other ammonium salts, the nitrate loses ammonia and becomes acid when exposed to the air or when heated. At ordinary temperatures the decomposition is represented by the equation:

$$(1)\qquad NH_4NO_3 = NH_3 + HNO_3$$

At temperatures above the melting-point, a secondary reaction is added to the first, as follows:

$$(2)\qquad NH_4NO_3 = N_2O + 2H_2O$$

When heated suddenly to a very high temperature, explosive decomposition occurs in accordance with the equation:

$$(3)\qquad 2NH_4NO_3 = 2N_2 + 4H_2O + O_2$$

If involved in a fire, its oxidising properties will add to the intensity of the conflagration.

Pure ammonium nitrate can be heated at 100°C. for a considerable time without appreciable decomposition (Findlay and Rosebourne, J.S.C.I. 1922, **41**, 58T), but in the presence of small percentages of organic matter, such as wood meal or starch, a slow evolution of carbon dioxide and nitrogen takes place.

The fused salt dissolves metallic zinc rapidly with evolution of considerable heat; lead also is rapidly oxidised; antimony, bismuth, nickel, copper and silver are oxidised slowly; arsenic, tin, iron, and mercury are not affected (J. P. Emmet, Amer. J. Sci. 1930, **18**, 255). According to W. R. E. Hodgkinson and A. H. Coote (Chem. News, 1904, **90**, 142) aluminium is not attacked by the fused salt. The same observers record that aqueous solutions of the salt react with metals as follows: cadmium is dissolved with the formation of nitrite in the cold; zinc and magnesium react slowly with the formation of double salts which are slightly soluble; lead becomes coated with lead nitrate; aluminium, silver and mercury are not perceptibly attacked. It is stated by some observers that iron is not attacked by ammonium nitrate solutions; E. Ramann (Ber. 1881, **14**, 1430) finds, however, that the salt is reduced in accordance with the equation:

$$2NH_4NO_3 + Fe = Fe(NO_3)_2 + 2NH_3 + H_2$$

It is stated that no hydrogen is actually evolved, as it is spent in reducing a further quantity of nitrate to nitrite.

Under certain conditions ammonium nitrate reacts with tin producing basic nitrates which are sensitive to heat and shock. Bassett and Durrant (J.C.S. 1922, **121**, 2, 630) found that ammonium nitrate reacts with copper or its alloys when exposed to air, forming deep blue crystals of cupric tetrammine nitrate, $Cu(NH_3)_4(NO_3)_2$, together with basic copper nitrate. The former is a comparatively sensitive explosive, and for this reason copper or its alloys must be excluded from any plant to be used with ammonium nitrate.

Explosibility.—While ammonium nitrate is not normally regarded as an explosive it can be detonated by means of a sufficiently powerful initiatory impulse. In 1921 a tremendous explosion occurred at Oppau in Germany at a factory which was engaged in the manufacture of fertilising salts containing a high percentage of ammonium nitrate (J.S.C.I. 1921, **40**, 381R). The cause of the explosion was somewhat obscure, but as it was known that explosives had been employed to disintegrate the hard, aggregated material it appears possible that the explosion may have been initiated in this manner, especially if the blasting charge had been fired in the neighbourhood of a pocket of the salts containing a much higher percentage of nitrate than was normal.

Explosions during the purification of ammonium nitrate have also occurred in America at Emporium, Pa. (Chem. Met. Eng. 1925, **32**, 595), and at Nixon, New Jersey (*ibid.* 1924, **31**, 383).

Aufschläger (Chem. Met. Eng. 1924, **30**, 619), discussing the explosibility of ammonium nitrate, states that it cannot be detonated at all with a No. 1 or No. 3 detonator, only partly with a No. 6, but completely with a No. 8 detonator.

When tested in Trauzl blocks the degree of fineness of the material was found to have an appreciable effect on the enlargement of the cavity, although decreasing with the density of loading. If, however, the crystals are very coarse so that the density of loading is very low, the blasting effect decreases materially. On the other hand material of the highest density, such as is obtained by fusing the salt and allowing it to solidify, is very difficult to detonate, the enlargement of the Trauzl block, using material of a density of 1·65, indicating that only partial detonation had been effected. If, however, only slight aggregation has occurred, such as may take place when moist ammonium nitrate is dried, the material may be detonated but not so easily as the loose crystals. The presence of moisture reduces the sensitiveness of ammonium nitrate to detonation, but a content of 5% or more is necessary to render it insensitive.

The lowest rate of detonation, namely 1,270 metres per second, was observed when the material was fired by means of a No. 8 detonator in a steel tube, and the highest, namely 2,440–2,460 metres per second, when a primer of picric acid in a lead tube was used.

Gawthorpe (Army Ord. 6, 47) has studied the influence of temperature on the explosibility of ammonium nitrate and found that under similar conditions with regard to confinement, diameter of charge, nature of primer, etc., the rate of detonation increases with rise of temperature, the effect being greatest between 80° and 120°C. The most effective primers in the order named were found to be tetryl, picric acid, trotyl 80/20, amatol and 75/10 ammonium nitrate dynamite. The rate of detonation as determined in Shelby seamless steel tubes and employing a loading density of 0·71 was found to vary from about 1,000 metres per second at 15°C. to approximately 1,700 m./sec. at 140°C.

Although ammonium nitrate adds to the intensity of a conflagration, Munroe (Chem. Met. Eng. 1922, **26**, 535) quotes several instances of fires in which ammonium nitrate was involved without any explosion occurring. He also found that when tested by the American method ammonium nitrate is insensitive to friction and no explosion occurred when a 20 kg. weight, falling through a height of 1 metre, impinged on nitrate confined between steel surfaces.

R. M. Cook (*ibid.* 1924, **31**, 231) carried out a series of experiments in order to ascertain the effect of various organic substances on the explosibility of ammonium nitrate. Samples of nitrate were treated with ½ and 1% of trotyl and 1 and 2% of petrolatum. When the samples were fired by detonators in iron tubes it was found that the maximum explosive effect was produced by the material containing 1% of petrolatum; 2% of this material caused less fragmentation than 1% of trotyl but probably had a more brisant effect. It is rather surprising to find that a non-explosive material gave a greater effect than trotyl which is itself a sensitive brisant explosive, and it is considered that the method of incorporation may possibly be the reason for this abnormal result.

Owing to its low sensitiveness to detonation ammonium nitrate cannot be used alone as an explosive and accordingly it is always mixed with a considerable proportion of sensitising materials such as trotyl, nitro-glycerin, etc. The amount of trotyl employed is seldom less than 20% in explosives of the amatol type since, if an appreciably less proportion is present, the trotyl-ammonium nitrate mixture is relatively insensitive to detonation.

Snelling and Wyler (U.S.P. 1749613) propose to sensitise mixtures of ammonium nitrate and trotyl, even when the latter is present to the extent of only 1%, by heating the mixture with metallic lead in the presence of methyl alcohol. The latter material is not essential, but it assists in shortening the time required to bring about the necessary reaction between the constituents of the mixture. The nature of the products formed is somewhat obscure, but it is stated that the resulting product is very easily detonated.

H. S.

AMMONIACUM. Ammoniacum is a gum resin obtained from an umbelliferous plant, *Dorema ammoniacum*, and possibly other species. The plant is widely distributed throughout Persia, and to a smaller extent in southern Siberia. The stems are punctured by small beetles, and the secretion contained in the schizogenous ducts of the cortex is exuded. The exudation dries on the stem in the form of tears or small lumps, the latter consisting of the smaller fragments which have become agglutinated and therefore are liable to contain extraneous matter such as woody fibre or earthy matter. Ammoniacum is hard and brittle at ordinary temperatures, softening on warming. It has a bitter, acrid taste and a somewhat unpleasant odour, due to the presence of a trace of essential oil. It consists of about 20 to 30% of gum, 50 to 75% of resin, with some water and traces of essential oil which, however, is sometimes present to the extent of 5 to 6%.

The only adulterant likely to be present is the so-called African gum ammoniacum, a gum resin which is derived from *Ferula tingitana*. It may be detected in the following manner. About 4 to 5 grms. are crushed and boiled for 15 minutes with 15 c.c. of hydrochloric acid. The liquid is cooled and filtered, and rendered alkaline with ammonia. Pure ammoniacum shows no fluorescence, but in the presence of African ammoniacum, asafœtida or galbanum resin a blue fluorescence results. An emulsion of ammoniacum with water does not give an orange-red colour with hypochlorites, but does so in the presence of African ammoniacum. A genuine ammoniacum should yield not less than 60% of extractive to 90% alcohol. A smaller amount indicates the presence of dirt and organic debris. The ash should not exceed 7%. The following analytical values have been recorded :

	Kremel.		Dieterich.		Beckurts and Bruche.	
	Persian.	African.	Persian (crude).	Persian (purified).	Persian (purified).	Persian (tears).
Sp.gr.	—	—	—	—	1·19–1·21	1·20
Ash %	—	—	—	—	0·79–4·47	3·84
Soluble in 96% alcohol . . .	—	—	46–88%	66–76%	59–68%	56%
Acid value of resin	100–112	59	57–105	79–135	69–80	70
Ester value of resin	30·6–50·5	123	64–91	73–98	19–38	35

Authentic samples of ammoniacum have been found to have the following characters :

No.	Essential oil %.	Water %.	Ash %.	Gum %.	Resin %.	Observer.
1	1·27	5·10	2·0	26·1	65·53	Plugge.
2	—	—	—	22·4	72·0	Bucholz.
3	—	—	—	18·4	68·6	Braconntot.
4	—	—	—	19·3	—	Moss.
5	1·43 to 6·68	0·81 to 3·27	2·02 to 3·27	—	47·2 to 69·2	Hirschsohn.

The essential oil obtained from the gum resin has the following characters : $d^{15\cdot5}$, 0·885–0·894 ; optical rotation, +1° to +3° ; n^{20}, 1·4723 to 1·4808 ; acid value, 1–4 ; ester value, 40 ; ester value after acetylation, 106. It contains terpenes, linalyl acetate, citronellyl acetate, a ketone termed doremone, doremyl acetate, cetyl alcohol and a dihydrosesquiterpene.

Ammoniacum is used in medicine to a very small extent, sometimes in chronic bronchitis. It facilitates expectoration and is mildly diuretic. E. J. P.

AMMONIOJAROSITE *v.* Jarosite.

AMMONITE *v.* Explosives, Coal Mine.

AMMONPULVER. This propellant powder is made by incorporating ammonium nitrate, 80–90 parts, with charcoal, 10–20 parts, and compressing the mixture into pellets having a density of about 1·4. In order to avoid fires during the drying process, due to contact of the pellets with air, Herbst (Chem.-Ztg. 1935, **59**, 744–5) recommends that carbon dioxide should be introduced into the drying chambers. This powder was used for a period in Austria, but was abandoned about 1896 in favour of ballistite. It can, however, be easily and cheaply made and was used by the Germans during 1914–1918. Ammonpulver gives no muzzle flash and causes practically no erosion of the gun barrel. On the other hand, it is difficult to ignite and is liable to give high pressures. Furthermore, the marked hygroscopicity of the powder is a distinctly objectionable property and special methods of protecting the pellets from moisture are necessary. H. S.

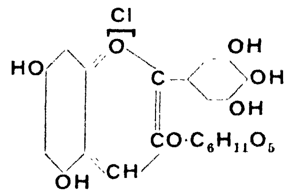
AMMOPHOS *v.* Ammonia, Ammonium Phosphate.

AMOSITE *v.* Asbestos.

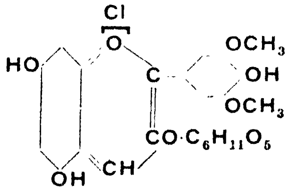
AMPANGABEITE. A rare-earth mineral from Madagascar. It is a tantalo-columbate (containing but little titanium) of uranium (UO_3 19·4%), iron, yttrium, thorium, etc. The crystals are orthorhombic and form sub-parallel groupings of large prisms of a brown colour and bright greasy lustre. Sp.gr. 3·97–4·29, depending on the degree of hydration, the material being optically isotropic. The mineral occurs associated with beryl, columbite, strüverite and monazite in pegmatite veins at Ampangabe, Ambatofotsikely, and Tongafeno. A considerable number of loose crystals have been collected from the weathered debris of the pegmatite (A. Lacroix, Min. de Madagascar, 1922, **1**, 376 ; **2**, 125). L. J. S.

AMPELOPSIN. The anthocyanin pigment of the berries of *Ampelopsis quinquefolia* Michx. (*Vitis hederacea* Ehrh.), isolated by Willstätter and Zollinger (Annalen, 1917, **412**, 213) as a crystalline hydrochloride, but not fully analysed. Easily soluble in methyl and ethyl alcohol and dilute aqueous acid, it gave a blue-violet colour with sodium carbonate, blue with sodium hydroxide and only a weak purple reaction with ferric chloride. Its "distribution number" or partition coefficient between amyl alcohol and aqueous acid (HCl) of 9·8 was normal for a monoglucoside. Hydrolysis yielded ampelopsidin (1 mol.) and glucose (1 mol.). The percentage of methoxyl and reaction with ferric chloride were abnormal for a monomethylated delphinidin, and Karrer and Widmer (Helv. Chim. Acta, 1927, **10**, 13) have now shown that this pigment is really a mixture of a small amount of delphinidin monoglucoside, $C_{21}H_{21}O_{12}Cl$ (I), together with its dimethylated derivative malvidin monoglucoside,

$C_{23}H_{25}O_{12}Cl$ (II).



I.



II.

(*See* Plant Pigments.) R. S.-M.

AMPHOTROPHIN. Trade name for hexamethylenetetramine camphorate.

AMYDRICAINE HYDROCHLORIDE *v.* Alypine.

AMYGDALIN, $C_{20}H_{27}O_{11}N$, m.p. 210°, $[\alpha]_D$ –42°, the best known of the cyanophoric glycosides, is found in bitter almonds and in the kernels of apricots, peaches, plums, and most fruits belonging to the Rosaceæ. About 18 g. of amygdalin may be obtained from 1 kg. of bitter almonds. It is widely used as a flavouring material and is the effective principle of essence of bitter almonds. It has been investigated for over 100 years. It has the structure :

$$\underbrace{\underset{\text{mandelonitrile}}{O_6H_5\cdot CH(CN)}\cdot O\cdot\underset{\text{glucose}}{C_6H_{10}O_5}}_{\text{mandelonitrile-}\beta\text{-glucoside}}\cdot\underbrace{O\cdot\underset{\text{glucose}}{C_6H_{11}O_5}}_{\text{gentiobiose}}$$

Yeast extract hydrolyses it to mandelonitrile glucoside and glucose ; almond extract hydrolyses it completely.

It has been synthesised from acetobromogentiobiose and ethyl-*dl*-mandelate (Campbell and Haworth, J.C.S. 1924, 1337).

Two other glycosides having the same composition as *d*-mandelonitrile glycoside (prunasin) are known, viz. sambunigrin and prulaurasin, which contain the *l*- and *dl*- forms of the nitrile respectively. For a fuller account, *see* E. F. and K. F. Armstrong, "The Glycosides," Longmans, 1931.

It has never been possible to obtain gentiobiose from amygdalin by hydrolytic means and for this reason it has taken a long time before the nature of the biose could be established. It was at one time termed amygdalose and thought to be other than gentiobiose.

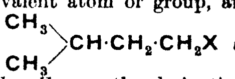
More recently this sugar has been obtained directly from the glycoside by catalytic hydrogenation in presence of palladium (Freudenberg, Toepffer, and Anderson, Ber. 1928, **61** [B], 1754). Similarly from amygdalin acetate by the same process Bergmann and W. Freudenberg (Ber. 1929, **62** [B], 2785) prepared gentiobiose-7-acetate. E. F. A.

AMYGDOPHENIN. Trade name for mandelyl-*p*-phenetidine,

$$C_2H_5O\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot C_6H_5,$$

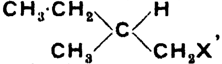
m.p. 140·5°. Antipyretic.

AMYL signifies the hypothetical monovalent radical C_5H_{11}—, derived from the three isomeric pentanes, C_5H_{12}, by removal of one hydrogen atom. Normal pentane may have one hydrogen atom substituted by a monovalent atom or group in three ways, secondary pentane or dimethylethylmethane may have one hydrogen atom substituted in four ways, and tertiary pentane or tetramethylmethane may have one hydrogen atom substituted in one way. There are thus eight series of derivatives of the radical "amyl." It is usual to designate as *amyl compounds* those of the type $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2X$, where X signifies a monovalent atom or group, and those of the type



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\cdot CH_2X$

as iso*amyl compounds*. Frequently derivatives of the type



$\begin{matrix}CH_3\cdot CH_2\\CH_3\end{matrix}\!>C<\!\begin{matrix}H\\CH_2X\end{matrix}$

, when in the optically active form, are referred to as *active amyl compounds*, as the commonly occurring active amyl alcohol belongs to this class. The other types of amyl derivatives are designated according to the usual methods of nomenclature in organic chemistry.

The amyl compounds of technical importance are either prepared from fusel oil or from the pentanes occurring in "natural gas" and are therefore rarely pure chemical individuals (*v.* ALCOHOLS PRODUCED BY SYNTHESIS FROM PETROLEUM).

Amyl Alcohols, $C_5H_{11}\cdot OH$. The eight theoretically possible structural isomerides are all known. Of these, three should also be capable of existing as optically active stereoisomerides. This has been effected in two cases, but not in the third, namely that of methyl*iso*propylcarbinol.

A very considerable amount of work has been done on the formation of the alcohols from the corresponding chloropentanes. This is fully reviewed by Ayres (Ind. Eng. Chem. 1929, **21**, 899). Any halogen is removed by distillation of the product over sodium (U.S.P. 1233333).

The physical properties of the various alcohols and derivatives have been fully described by Lievens (Bull. Soc. chim. Belg. 1924, **33**, 122), Munch (J. Amer. Chem. Soc. 1926, **48**, 994), and Simon (Bull. Soc. chim. Belg. 1929, **38**, 47).

***n*-Amyl Alcohol,**

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$$

(Pentanol). This alcohol was prepared in an impure state by Schorlemmer (Annalen, 1872, **161**, 269) from crude pentane. Wischnegradsky (Annalen, 1878, **190**, 328) concluded that it was present in commercial amyl alcohol, but this has been shown to be incorrect (Tissier, Bull. Soc. chim. 1893 [iii], **9**, 100).

It is a colourless liquid of fusel oil odour ; b.p. 137·7° ; d^{20}_{20} 0·8168. It is best prepared by reducing valeramide with sodium and alcohol (Chem. Zentr. 1904 [ii], 1698), or by a similar reduction of ethyl-*n*-valerate or ethyl-*n*-propylacetoacetate (G.P. 164294, 1905 ; *see also* Biochem. Z. 1914, **62**, 470 ; and Annalen, 1871, **159**, 70 ; 1886, **233**, 253).

***iso*Butylcarbinol, $(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot OH$** (3-methylbutanol), ordinary iso*amyl alcohol, fermentation amyl alcohol*, is the chief constituent of most fusel oils. It also occurs as angelic and tiglic esters in oil of camomile (Annalen, 1879, **195**, 99). It constitutes from 50 to 85% of technical amyl alcohol. (For further details as to the isolation of *iso*amyl alcohol from fusel oil, etc., *see* below under Fusel Oil.)

It is a colourless liquid possessing a characteristic cough-provoking odour ; b.p. 131·4°/760 mm., 46·8°/14·2 mm. It freezes at −134°, and melts at −117·2° ; d^0_4 0·823. It is soluble in 50 parts of water at 13·5°. One litre of water dissolves 34·7 c.c. *iso*amyl alcohol ; 1 litre of the alcohol dissolves 22·14 c.c. water.

It may be prepared synthetically by reducing *iso*valeric acid (from *iso*butylalcohol), or better, by the action of trioxymethylene on *iso*butyl magnesium bromide (Locquin, Bull. Soc. chim. 1904 [iii], **31**, 599). It is a strong poison both to human beings and to bacteria. It is about eight times as poisonous to man as ethyl alcohol (Macht, J. Pharmacol. 1920, **16**, 1).

Ebert (Österr. Chem.-Ztg. 1925 **28**, 176) describes precautions to be taken against its poisonous effects when used industrially.

Derivatives.—*Urethane*, m.p. 64·5° ; *phenyl urethane*, m.p. 54° ; *phenyl carbamate*, m.p. 55°. When treated with thionyl chloride iso*amyl chlorosulphinate*, b.p. 127°–128°/15 mm., is obtained (Voss and Blanke, Annalen, 1931, **485**, 258).

The alcohol is used under the trade name of *Pentasol* as a solvent in nitrocellulose lacquers

(Wilson and Worster, Ind. Eng. Chem. 1929, **21**, 592) and also finds extensive application in the "Gerber" milk test. Its use in this latter case is only permissible when it conforms to a given specification (Goy and Janisch, Z. Nahr. Genussm. 1925, **50**, 373 ; Houston, Analyst, 1933, **58**, 151 ; Golding, *ibid.*, pp. 276, 531).

Secondary Butylcarbinol,

$$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}OH$$

(2-methylbutanol). Active amyl alcohol, the second constituent of commercial amyl alcohol, is a colourless liquid of similar odour to the above. The vapour does not provoke coughing, but has greater stupefying effects ; b.p. 128° ; d_4^{20} 0·816 ; $[\alpha]_D^{20}$ −5·90°.

The active alcohol, in spite of its lævorotation, is more correctly termed *d*-amyl alcohol, on account of its genetic relationships with *d*-*iso*leucine and with *d*-valeric acid. The oxidation of the alcohol yields pure *d*-methylethylacetic acid. For the methods of isolating the pure active alcohol from fusel oil, *v. infra*, under Fusel Oil. It should be noticed that all technical amyl compounds contain variable amounts of the active amyl derivatives.

Derivatives.—*Urethane,* m.p. 61° ; *phenyl carbamate,* m.p. 30° ; *3-nitrophthalate,* m.p. 114°.

The active alcohol is partially or wholly racemised by heating above 200°, more especially when in the form of sodium amylate or in the presence of salts soluble in the alcohol (J.C.S. 1897, **71**, 256 ; Proc. Roy. Soc. 1869, **17**, 308). The racemic alcohol has been synthesised by the reduction of natural or synthetic tiglic aldehyde (Herzig, Monatsh. 1882, **3**, 122), and by the action of *sec*-butyl magnesium bromide on trioxymethylene (Freundler and Damond, Bull. Soc. chim. 1906 [iii], **35**, 110) ; a 67% yield is obtained by blowing formaldehyde into an ethereal solution of *sec*-butyl magnesium bromide (Wood and Scarf, J.S.C.I. 1923, **42**, 13T). It has b.p. 128°/749 mm. Its acid *m*-nitrophthalate melts at 117°. A mixture of racemic with *l*-amyl alcohol was obtained by Le Bel (Bull. Soc. chim. 1878 [ii], **31**, 104).

Tertiary Butylcarbinol, $(CH_3)_3C{\cdot}CH_2{\cdot}OH$ (2 : 2-dimethylpropanol). This alcohol is a volatile solid melting at 52°–53°, has a pleasant turpentine-like odour, b.p. 113°–114°, and exhibits all the characteristic properties of a primary alcohol.

It has been prepared by reduction of trimethylacetyl chloride also, in poor yields, by the hydrolysis of chlorinated tetramethylmethane and by the action of the suitable Grignard reagent on paraformaldehyde or methyl formate (Tissier, Ann. Chim. Phys. 1893 [vi], **29**, 340 ; Samec, Annalen, 1907, **351**, 256 ; Bouveault, Compt. rend. 1904, **138**, 985, 1108). The action of nitrous acid upon *βββ*-trimethylethylamine yields not this alcohol but the isomeric dimethylethylcarbinol (Tissier, Compt. rend. 1891, **112**, 1065).

Methyl-*n*-propylcarbinol,

$$CH_3{\cdot}CH(OH){\cdot}C_3H_7$$

(pentanol-2), *secondary amyl* alcohol. This is a colourless liquid of b.p. 119°, and d_{20}^{20} 0·8102. It is prepared by treatment of Δ^2-pentene with sulphuric acid (product mixed with 30% of 3-pentanol) and by the reduction of methyl-*n*-propyl ketone by means of sodium amalgam or, better, by the method of Sabatier and Senderens (Chem. Zentr. 1903, II, 708). The best method, however, is by the action of propyl magnesium bromide on acetaldehyde (76% yield) (Wood and Scarf, J.S.C.I. 1923, **42**, 13T).

This alcohol is racemic. Le Bel, using *Penicillium glaucum,* obtained a lævorotatory specimen (Compt. rend. 1879, **89**, 312). Pickard and Kenyon (J.C.S. 1911, **99**, 45), by crystallisation of active alkaloid salts of the hydrogen amyl phthalates, obtained the pure *d*-alcohol ; b.p. 118·5°–119·5° ; $d_4^{12\cdot3}$ 0·8169 ; $[\alpha]_D^{20}$ +13·70°.

Methyl*iso*propylcarbinol,

$$CH_3{\cdot}CH(OH){\cdot}CH(CH_3)_2$$

(4-methylbutan-2-ol), a colourless liquid with a fusel oil odour ; b.p. 113°, does not freeze at −33°, d_{19}^{19} 0·819. Hydrogen halides react with it very slowly to produce only tertiary compounds, such as $C_2H_5(CH_3)_2CCl$. It has been prepared by the reduction of the corresponding ketone and, in good yield, by the peculiar action of zinc dimethyl upon bromoacetyl bromide or chloroacetyl chloride (Winogradow, Annalen, 1878, **191**, 127 ; Bogomelez, *ibid.* 1881, **209**, 87). It may also be obtained by the interaction of methyl magnesium bromide and *iso*butylene oxide, chloroacetone, or chloroacetyl chloride (Henry, Compt. rend. 1907, **145**, 21). This alcohol is racemic and has not yet been resolved.

Diethylcarbinol, $C_2H_5{\cdot}CH(OH){\cdot}C_2H_5$ (pentan-γ-ol). This is a colourless liquid having the usual amyl alcohol odour ; b.p. 114°–115° at 749 mm. ; $d^{14\cdot7}$ 0·8271.

It is prepared by the action of ethyl formate on zinc ethyl (Wagner and Saytzeff, Annalen, 1875, **175**, 351), or on ethyl magnesium bromide (Chem. Zentr. 1901, II, 623).

Derivative.—*Phenyl urethane,* m.p. 48°–49°.

Ethyldimethylcarbinol, $C_2H_5{\cdot}C(CH_3)_2OH$ (2 : 2-dimethylpropanol). This alcohol, commonly known as *tertiary amyl alcohol* or *amylene hydrate,* is a colourless liquid possessing an odour resembling that of camphor ; b.p. 101·5°–102° ; m.p. −12° ; d_{15}^{15} 0·8144.

It has been prepared synthetically by the interaction of propionyl chloride and zinc dimethyl (Wischnegradsky, Annalen, 1878, **190**, 328). It is produced commercially by treating amylene with aqueous sulphuric acid, and subsequently boiling the solution (Adams, Kamm and Marvel, J. Amer. Chem. Soc. 1918, **40**, 1950). Trimethylethylene, the chief constituent of commercial amylene, is thus quantitatively converted into tertiary amyl alcohol, which is employed medicinally as a hypnotic.

The following test is described by Ekkert (Pharm. Zentr. 1925, **66**, 599). 0·5 c.c. of a 5% alcoholic solution of the alcohol is mixed with 5 c.c. conc. sulphuric acid and a 5% solution of tartaric acid poured carefully into the tube. A rose-coloured ring is formed at the interface.

Fusel Oil is the source of all commercial amyl compounds. It is a yellow or brownish liquid possessing a nauseating taste and a characteristic unpleasant, cough-provoking odour and burns with a bright flame. It boils from 80° upwards, but chiefly between 128° and 132°, and has a density of about 0·83.

The chief source of commercial fusel oil is the residue in the refining of the crude spirit from the fermentation of potatoes or molasses. The separation is effected by fractionating the fermented liquor, usually in a continuously operating plant (*see* under ALCOHOL). When the ethyl alcohol content of the liquid has fallen to 15%, the fusel oil may be removed from the surface, where it separates as an oily layer. Crude spirit after fractionation may contain 95% of ethyl alcohol, and usually about 0·4% of fusel oil. Brandy contains at the most only traces, but the spirits having the most pleasing aroma, those from corn or fruit, *e.g.* cherries, etc., may contain up to 0·6% or more of fusel oil, partly in the form of esters. The presence of the fusel oil may increase the intoxicating properties of the spirit, but the harmful effects of excessive spirit drinking seem to be caused mainly by ethyl alcohol.

The chief constituent of most fusel oils is the mixture of *iso*amyl alcohol and active (lævorotatory) *d*-amyl alcohol, which constitutes 65–80% of the whole, and which is sold as commercial amyl alcohol of b.p. 128°–132°. The proportions in which these two amyl alcohols occur vary considerably, as Marckwald pointed out, according to the source of the specimen. Ordinary corn or potato amyl alcohol contains from 13·5 to 22% of the active isomeride, while the amyl alcohol from molasses fusel oil contains from 48 to 58% of the lævorotatory alcohol. Besides the amyl alcohols, ordinary fusel oils contain usually from 15 to 25% of *iso*butyl alcohol (b.p. 108°), and from 4 to 7% of *n*-propyl alcohol (b.p. 97°). But the fusel oils from wines may contain large quantities (as much as 50% of the whole) of *n*-butyl alcohol. That produced by the Weizmann Fermentation Process is said to contain 65% of butyl alcohol.

In addition to these main constituents there are always present in small quantities some or all of the following : hexyl and heptyl alcohols, furfurol, acetaldehyde, *iso*butyl and valeric aldehydes, ammonia and amines, pyridine, pyrazine derivatives, traces of all the fatty acids up to capric acid in the form of ethyl, amyl, or œnanthyl esters, terpene and terpene hydrate. Palmitic acid or ester has also been found. Kumamoto (J. Chem. Soc. Japan, 1932, **53**, 30) records analyses of a number of different fusel oils.

The formation of fusel oil in fermentation has been explained by Ehrlich (Ber. 1906, **39**, 4072 ; 1907, **40**, 1027, 2538 ; 1912, **45**, 1006 ; Biochem. Z. 1911, **36**, 477 ; *see also* Biochem. Z. 1907, **3**, 121 ; 1908, **10**, 490). Ehrlich has shown that the addition of leucine and *d*-*iso*leucine, in the form of, *e.g.*, hydrolysed egg albumen, during the fermentation process, results in a largely increased yield of amyl alcohols. This is made the basis of a technical method (G.P. 177174). Leucine, from egg albumen, can also be converted by dry distillation into amylamine (G.P. 193166), and thence into a mixture of amyl alcohols similar to that occurring in fusel oil. The formation and origin of fusel oil have also been discussed by Mumme (Woch. Brau. 1924, **41**, 137) and Lühder (Z. Spiritusind. 1925, **48**, 297).

Detection and Estimation.—Fusel oil is best detected in spirits by rubbing a little of the liquid between the hands, when the ethyl alcohol evaporates and the residue reveals itself by its odour. When a large quantity is available for the estimation, it may be accomplished by subjecting the material to fractional distillation ; modified fractionation tests have been described by Lampe (Z. Spiritusind. 1928, **51**, 30) and Kilp and Lampe (Z. angew. Chem. 1928, **41**, 1163). For ordinary purposes the usual method depends on the extraction of the fusel oil from a 30% ethyl alcohol solution by means of chloroform, the increase in volume of the latter being observed (*see* Ehrlich, Ber. 1907, **40**, 1031 ; Pringsheim, Biochem. Z. 1907, **3**, 233). For another valuable method, *see* Abderhalden's "Handbuch der biochemische Arbeitsmethoden," ii, 11. A method of estimation has recently been proposed by Budagjan and Ivanova (Z. Unters. Lebensm. 1932, **63**, 200) in which the alcohol is oxidised with alkaline silver nitrate and the aldehyde produced is determined colorimetrically (*v.* FUSEL OIL).

Uses.—Fusel oil and commercial amyl alcohol are valuable solvents for resins, fats, and oils ; amyl alcohol, being much more useful for these purposes than ethyl alcohol, is therefore indispensable in industry. It is much used in the nitrocellulose smokeless powder and lacquer industries. It has been proposed as a raw material for the production of synthetic rubber (Perkin, J.S.C.I. 1912, **31**, 616). It is also used as a source of valeric acid, and Piotrowski (Przemysł Chem. 1929, **13**, 413) has suggested a two-stage process, firstly vapour-phase oxidation of the alcohol over copper gauze at 370°–390°, followed by treatment with potassium permanganate. The overall yield is 39%.

Preparation of iso*Amyl and* d-*Amyl Alcohol from Fusel Oil.*—This separation was first partially effected by Pasteur (Annalen, 1855, **96**, 255) by the fractional crystallisation of the barium salts of the amyl sulphuric acids. Le Bel went further, using the fact that conversion of the alcohols into the chlorides by hydrogen chloride left a more active residue than the original mixture (Bull. Soc. chim. 1874 [ii], **21**, 542 ; 1876 [ii], **25**, 545). Marckwald finally isolated the two alcohols in a state of chemical purity (Ber. 1901, **34**, 479, 485 ; 1902, **35**, 1595, 1602 ; 1904, **37**, 1038), by fractional crystallisation of the 3-nitrophthalic esters and also by using Pasteur's method. All the pairs of derivatives of the two components of natural amyl alcohol examined by Marckwald formed mixed crystals.

To obtain *iso*amyl alcohol a potato amyl alcohol containing 80% of *iso*amyl alcohol is converted at once into the 3-nitrophthalic ester, m.p. 95°, which is quickly purified by recrystallisation.

To obtain *d*-amyl alcohol (lævorotatory), the amyl alcohol from molasses containing at least 50% of the required compound is saturated with dry hydrogen chloride at 0°, and heated in an autoclave for five hours at 110°. On distillation of the product a liquid is obtained containing 80% of the active alcohol as chloride. This is then converted into the 3-nitrophthalate and recrystallised from benzene until the melting-point of the compound is 114°. The two alcohols are very easily obtained from the acid nitrophthalic esters by hydrolysis.

Amyl Acetate, $C_5H_{11}\cdot OAc$. A colourless neutral mobile liquid having a penetrating odour resembling that of jargonelle pears ; b.p. 138·5°–139° ; d_4^{15} 0·875. Is easily inflammable, sparingly soluble in water, but readily so in organic solvents. For its preparation, 1 part of commercially pure amyl alcohol, 1 part of glacial acetic acid and ½ part of concentrated sulphuric acid are heated at 100° for five hours, the mixture poured into water and the oil separated. The oil is shaken with a strong aqueous solution of sodium carbonate, dried and distilled. (*See also* Senderens, Compt. rend. 1911, **152**, 1671 ; and B.P. 4669, where fusel oil, hydrochloric acid, and calcium acetate are used.) Since the growth of the "natural gas" industry in the United States, amyl acetate is chiefly manufactured in that country by heating monochloropentane (formed by direct chlorination of pentanes) with sodium acetate under pressure (Brooks, Smith, and Essex, Ind. Eng. Chem. 1918, **10**, 511 ; Koch and Burrell, Ind. Eng. Chem. 1927, **19**, 442 ; U.S.P. 1302583, 1374666).

The alcoholic solution is largely used under the name of "Jargonelle Pear Essence," for flavouring confectionery. Amyl acetate is an excellent solvent for nitro-cotton, camphor, tannin and resins, and finds extensive use in the celluloid and varnish industries. It is also used in the manufacture of photographic films and of smokeless powder. It is recommended as a standard oil in photometry (Williams, J.S.C.I. 1885, **4**, 262). Hannotte (Bull. Soc. chim. Belg. 1926, **35**, 86) has described the azeotropic mixtures with water and finds one to contain 32·6% water, boiling at 142°. The ester is sometimes marketed under the trade name of "Pentacetate." A report on cases of industrial poisoning by amyl acetate is made by Koelsch (Z. angew. Chem. 1920, **33**, I, 1).

Synthetic Amyl Alcohols (*Pentasol*, b.r. 112°–140°, sp.gr. ·812–·820 at 20°), (*Peramyl alcohol*, b.r. 90°–160°, sp.gr. ·883) are used as general solvents ; and the following esters are used extensively in industry as solvents and plasticisers.

Ester.	Boiling range °C.	Sp.gr.	Use.
Acetate (*pentacetate* or *pentasol* acetate)	138–142	·875	Solvent.
Benzoate . . .	260–261	·994 to 1·01	Plasticiser.
Borate . . .	250–260	·865	Solvent for gums.
Chloride . . .	85–109	·88	Solvent.
Formate . . .	110–130	·88–·885	Solvent.
Lactate . . .	*c.* 210	·957–·960	Paint industry.
Oxalate . . .	*c.* 265	·97	Plasticiser.
Phthalate (*Placidol A*)	336–342	1·026	Yields elastic films highly resistant to weather.
Propionate . .	140–170	·870–·873	Brush lacquers.
Salicylate (*Plastolin II*)	—	—	Plasticiser.
Stearate . . .	*c.* 360	·860	Plasticiser.
Tartrate . . .	*c.* 400	1·05–1·06	Plasticiser.

***n*-Amylamine** is obtained by reduction of butyl cyanide with sodium in butyl alcohol (Suter and Moffett, J. Amer. Chem. Soc. 1934, **56**, 487).

Amyl Bromide. *iso*Amyl bromide may be prepared, in 85–90% yield, by treatment of the alcohol with a mixture of hydrobromic and sulphuric acids obtained by reduction of bromine with sulphur dioxide (Kamm and Marvel, J. Amer. Chem. Soc. 1920, **42**, 299). It has b.p. 116°–120°. When treated with sodium under reflux it yields di-*iso*amylene, b.p. 160° (Timmermans and Hennaut-Roland, Anal. Fís. Quím. 1929, **27**, 460). *n*-Amyl bromide, b.p. 128°, has been prepared by Karvonen (Acad. Sci. Fennicæ, 3A, 1). (*See also* Main, Bur. Stand. J. Res. 1932, **9**, 457.)

Amyl Chlorides have been produced chiefly by direct chlorination of pentanes obtained in "natural gas" (*see* references under Amyl Acetate), but may be obtained by boiling under reflux a mixture of 1 mol. alcohol with 2 mols. conc. hydrochloric acid and 2 mols. anhydrous zinc chloride, and separating the product by distillation (Norris and Taylor, J. Amer. Chem. Soc. 1924, **46**, 753) or by treatment of secondary Grignard reagents with cyanogen chloride (Grignard and Ono, Bull. Soc. chim. 1926 [iv], **39**, 1589).

Amylenes are the corresponding olefinic hydrocarbons C_5H_{10} and are generally prepared by dehydration (catalytic or otherwise) of the alcohols. Various members of the group have been described by Wischnegradsky (Compt. rend. 1878, **86**, 973) ; Adams, Kamm and Marvel (J. Amer. Chem. Soc. 1918, **40**, 1950); Senderens (Compt. rend. 1920, **171**, 916), and Whitmore and Simpson (J. Amer. Chem. Soc. 1933, **55**, 3809).

Amyl Ether, $C_5H_{11}{\cdot}O{\cdot}C_5H_{11}$. A colourless liquid possessing a pleasant pear-like smell; b.p. 172·5°–173°; d^{15} 0·7807. It is prepared by heating the alcohol to its boiling-point with 1/10 part of concentrated sulphuric acid (G.P. 200150), or with 1/10 part of amyl iodide in an autoclave at 250°. It may also be obtained by heating amyl alcohol under reflux with diluted sulphuric acid followed by distillation in steam (Popelier, Bull. Soc. chim. Belg. 1923, **32**, 179; *see also* Zappi and Degiorgi, Anal. Asoc. Quím. Argentina, 1930, **18**, 210). It is used as a solvent in the Grignard reaction, for fat extraction, for perfumes, alkaloids, in the varnish industry, and therapeutically. Popelier (*l.c.*) gives the b.p. of the *n*-isomer as 187·9°. The *secondary* derivative is described by Senderens (Compt. rend. 1925, **181**, 698). It is formed by heating the alcohol with 2·5% by weight of concentrated sulphuric acid at 120°. B.p. 162°, *d* 0·775.

Amyl Fluorides, *n*- b.p. 62·8°, *iso*- b.p. 53·5°, are described by Swairts (Bull. Soc. chim. Belg. 1921, **30**, 302) and are prepared by the action of mercury fluoride on the corresponding amyl bromide or iodide.

Amyl Formate, $HCO{\cdot}OC_5H_{11}$, a fragrant liquid of b.p. 123·3° and d_4^0 0·8944, prepared from fusel oil and formic acid or from fusel oil, glycerol, and oxalic acid. It is used in the synthetic fruit essence industry and in the laboratory in the preparation of oxymethylene derivatives.

***tert*-Amyl Hypochlorite,** b.p. 76°/752 mm., is a yellow mobile liquid with an irritant lachrymatory vapour, formed by passing chlorine through an alkaline solution of the alcohol. It decomposes at the boiling-point but the *primary* and *secondary* hypochlorites are much more unstable (Chattaway and Backeberg, J.C.S. 1923, **123**, 2999).

***d*-Amyl Mercaptan, $C_5H_{11}{\cdot}SH$.** A liquid of b.p. 119°–121°, was prepared in a state of purity from fusel oil by Vorocek and Vesely (Ber. 1914, **47**, 1515). Amyl mercaptan has also been formed by heating the corresponding *iso*-thiourea (Backer and others, Rec. trav. chim. 1932, **51**, 1166). The 3 : 5-dinitrobenzoyl derivative (m.p. *n*- 39–40°, *iso*- 42°–43°) and 3-nitrophthalic esters (m.p. *n*- 131°–132°; *iso*- 144°–145°) have been described (Wertheim, J. Amer. Chem. Soc. 1929, **51**, 3661). It is used to resolve racemic arabinose into its optically active components.

***iso*Amyl Nitrite, $C_5H_{11}O{\cdot}NO$.** A yellow neutral or feebly acid liquid, possessing a fruity odour; b.p. 97°–99°; d^{15} 0·870–0·880. It burns with a brilliant flame. It should be kept protected from light, but in any case it is best either freshly prepared or repeatedly fractionated before use. The vapour should not be inhaled. It has been prepared by passing nitrous fumes into amyl alcohol kept at 70°–90° (Balard, Ann. Chim. Phys. 1844 [iii], **12**, 318; Williams and Smith, Pharm. J. 1886, 499). Bouveault and Wahl passed nitrosyl chloride into a dry mixture of pyridine and amyl alcohol (Compt. rend. 1903, **136**, 1563). It is best prepared by treating the alcohol with a solution of sodium nitrite followed by sulphuric acid (Adams and Kamm, J. Amer. Chem. Soc. 1918, **40**, 1281). It is used in the preparation of diazo and *iso*nitroso compounds or nitroso chlorides, and as the "amylium nitrosum" of medicine for the treatment of epilepsy, asthma, angina pectoris, etc., since it reduces blood pressure and retards the pulse.

Tertiary Amyl Nitrite,

$$(CH_3)_2(C_2H_5){\cdot}C{\cdot}O{\cdot}NO$$

(Bertoni's "Amylonitrous Ether"), has been used as a substitute for ordinary amyl nitrite, its action being stronger in degree and more lasting. It is a yellow liquid of weak camphoraceous odour and peppermint taste; b.p. 93° (J.S.C.I. 1889, **8**, 1003). The physiological action has been studied by Krantz (Pharm. Weekblad, 1932, **69**, 101) and Schott (Arch. exp. Path. Pharm. 1920, **16**, 1).

Wilson and Yang (Chinese J. Physiol. 1930, **4**, 391) record the boiling-points of four isomeric amyl nitrites as follows: *n*- 51·5°–52·1°/132 mm.; *iso*- 98·2°–99·2°/760 mm.; *sec*- 96·0°–96·5°/760 mm.; *tert*- 62·0°–63·0°/345 mm. The densities and refractive indices are also given.

***n*-Amyl Orthosilicate** is formed when the alcohol is treated with silicon tetrachloride below 0°. It has b.p. 145°–150°/3 mm., d_4^{25} 0·8933 (Dearing and Reid, J. Amer. Chem. Soc. 1928, **50**, 3058).

Amyl Phosphate is produced in 63% yield by the action of phosphoryl chloride on the alcohol in pyridine (Noller and Dutton, J. Amer. Chem. Soc. 1933, **55**, 424), or by treating sodium amyloxide in toluene with phosphoryl chloride (v. Falkenhausen, Biochem. Z. 1932, **253**, 152). The ester has b.p. 158°–163°/6 mm.

Amyl Salicylate, $C_5H_{11}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$ (*Amylenol*), is a colourless refractive liquid, b.p. 250° (with decomposition), and 115°/2 mm.; d^{15} 1·065. It is produced by passing dry hydrogen chloride into a saturated solution of salicylic acid in amyl alcohol, and after some hours pouring into water and working up as usual. It is used medicinally as an antirheumatic and in the perfume and fruit essence industry.

Amyl Sulphate has been obtained by heating a mixture of the sulphite and chlorosulphonate with or without zinc chloride (Barkenbus and Owen, J. Amer. Chem. Soc. 1934, **56**, 1394; Levaillant, Compt. rend. 1933, **197**, 335), and also as a by-product in the preparation of the ether (Popelier, Bull. Soc. chim. Belg. 1923, **32**, 179). *n*-Amyl sulphate has b.p. 117°/2·5 mm.

Amyl Sulphide may be prepared in the usual way. The addition compounds of the *iso*-derivative with various mercury salts are described by Faragher, Morell and Conway (J. Amer. Chem. Soc. 1929, **51**, 2774).

E. G. N.

AMYL ESTERS. A number of amyl esters are used in perfumery, most of which have not very characteristic odours, other than what may be termed fruity. Several are used in the manufacture of artificial fruit essences, amyl acetate being the well-known artificial pear oil. Amyl benzoate, $C_6N_5{\cdot}COO{\cdot}C_5H_{11}$, b.p. 262°, sp.gr. at 20° 0·994, ref. index 1·4910, has an amber odour and is used in "oriental" perfumes and as a solvent and fixative for artificial musk. Amyl salicylate,

$$C_6H_4(OH)COO{\cdot}C_5H_{11},$$

sp. gr. 1·055, b.p. 152°/15 mm., 280°/760 mm., ref. index 1·5070, is more useful than any other amyl ester in perfumery. It is known as trèfle, or artificial orchid, and forms the basis of that type of perfume. It is also largely used in soap perfumery. E. J. P.

α-AMYL-CINNAMALDEHYDE,

$$C_6H_5{\cdot}CH : C(C_5H_{11})CHO,$$

was originally introduced to the perfumer under the name *flosal*. It is a most valuable synthetic having a flowery jasmin odour, and is much employed in the manufacture of this type of floral perfume. Sp.gr. 0·956–0·961, ref. index 1·515 to 1·519. Commercial samples vary somewhat outside these limits. E. J. P.

α- and β-AMYLAN. The term amylan is used for certain cereal gums of unknown constitution.

Horace Brown (Trans. Guinness Research Laboratory, 1906, 317, where there is a full account of amylan) finds that when barley gum is steeped in malt extract it swells up and undergoes gradual liquefaction and solution, and in a few days its colloidal nature is lost. This is one of the most significant changes which mark the conversion of barley into malt.

To prepare "amylans" in quantity the finely divided grain is boiled with water, treated with malt extract at 50°–55° for an hour to liquefy the starch, boiled again, and filtered. The filtrate is concentrated in vacuum to sp.gr. 1·060, and three volumes 80% alcohol (by volume) added gradually. The crude amylans are precipitated in large white flocks free from dextrin and have no cupric reducing power. Corrected for ash and nitrogen they amount, on a number of dry barleys, to about 9·6%, and have $[\alpha]_D$ +62° to +73° (Horace Brown, *l.c.*). This amount practically accounts for the whole of the missing constituents of the soluble portion of barley after hydrolysis with malt extract.

On hydrolysis about 60% of glucose is formed, together with arabinose, xylose, and an unknown substance of low rotation and reducing power.

The above dextrorotatory amylan includes everything insoluble in 62% alcohol. By a variation of the method of preparation a carbohydrate, $[\alpha]_D$ −100·34°, corresponding to Wroblewski's araban, was obtained.

Earlier work on amylan was done by O'Sullivan.

It is obvious that the "amylans" require further investigation. According to O'Sullivan (Chem. Soc. Trans. 1882, **41**, 24) it is probably owing to the presence of amylan that unmalted barley cannot be satisfactorily employed in the preparation of beer. Malted grain does not contain it. Distillers using raw grain (oats and barley) have at times much difficulty in separating the wort (solution of sugars, etc.) from the grains (undissolved portion of the grain employed) in consequence of the presence of amylan in quantity, the barleys and oats of some seasons containing much more of it than at other times. E. F. A.

AMYLARINE. *iso*Amyltrimethylammonium hydroxide.

AMYLASE, the enzyme which hydrolyses starch, is widely distributed in animals and plants. In brewing, where it is better known by the older name of diastase, it plays an important rôle which is treated under that heading, this account being confined to its biochemical properties discussed in relation to recent work.

The p_H of animal amylase is around 7, that of malt diastase about 5·2.

It is becoming customary to accept diastase as containing two components and to divide amylases into two groups distinguished as α- and β-. The former produce α-maltose, the latter β-maltose from starch. Kuhn (Annalen, 1925, **443**, 1) found that β-maltose was primarily produced by malt amylase, whereas pancreatic amylase or taka-diastase yielded α-maltose. Kuhn's theory demands either the existence of two different starches or the alternate existence of two different α- and β-glycoside linkages in starch, which is in conflict with Haworth's formula for starch. β-Amylase is obtained best from unsprouted barley; α-amylase is best made from a malt extract precipitated with 60% alcohol and then heated at 70° for fifteen minutes, when the β-amylase is destroyed.

The optimal p_H for α-amylase is 5·1, and for β-amylase 4·3. A normal barley extract (20 grms. of barley and 100 c.c. of distilled water) has a p_H of 6·3, its β-amylase action being increased 17 times by displacement of the p_H to 4·3. An extract of barley after treatment of the grain with papain contains, at the optimal p_H, twice the amount of β-amylase as an ordinary aqueous extract. It is concluded that by changes of p_H conversion of α- into β-amylase occurs (Polak and Tychovski, Biochem. Z. 1928, **192**, 463).

Acting on Lintner's soluble starch β-amylase forms β-maltose up to 64% of the theoretical. The iodine coloration persists; liquefaction runs parallel with hydrolysis.

Under similar conditions α-amylase quickly forms 36% of α-maltose, whilst the iodine reaction disappears; liquefaction is more rapid than hydrolysis.

α-Amylase is adsorbed preferentially on starch at p_H 4·4, β-amylase being left behind (Holmbergh, Biochem. Z. 1933, **266**, 203). It is also selectively adsorbed by the amyloses, dextrins and glycogens. Giri (Current Sci. 1933, **2**, 128) claims a partial separation by centrifuge methods.

The crystalline hexasaccharide obtained by means of pancreatic α-amylase acting on erythroamylose gives no colour with iodine and is attacked by both α- and β-amylases to give α- and β-maltose respectively (Waldeschmidt-Leitz and Reichel, Z. physiol. Chem. 1934, **238**, 76).

The saccharifying power of amylase is the function of the β-amylase, whereas the liquefying power is related to the α-enzyme.

β-amylase is identical with the preformed diastase of resting barley (Hopkins, Cope, and Green, J. Inst. Brew. 1933, **39**, 487).

It is found (Petit and Richard, Compt. rend. 1925, **181**, 575) that when allowed to act at the optimum hydrogen-ion concentration (p_H 4·2) amylase dissolved in boiled water is the most potent ; the same holds in more acid media, but in alkaline media amylase dissolved in water through which hydrogen is passed is the most active ; in each case amylase dissolved in aerated water is the least active. An algebraic relationship between the hydrogen-ion concentration of the medium and the amount of maltose produced has been observed, different equations being necessary on either side of an inflexion point at p_H 5·5–6·4. Saccharification of starch does not proceed in acid media, whilst production of maltose is retarded, but not completely stopped, in alkaline media.

The α-diastase and nitrogen contents of samples of oats, wheat, rye, and barley have been tabulated by Synievski (Biochem. Z. 1928, **182**, 457). The number of diastatic units per milligram of nitrogen decreases in the following order : wheat, barley, rye, oats. About one-third of the diastase of wheat and barley, four-fifths of that of rye and the whole of that of oats can be extracted by water. The proportionality between the number of α-diastase units and the nitrogenous material rendered extractable by the action of papain is only slight. Agreement is approximate for barley and wheat, but deviation is considerable with rye and oats.

The knowledge of activators and inhibitors of amylase is in an imperfect state.

According to Purr (Biochem. J. 1934, **28**, 1141) ascorbic acid activates the β-type of animal amylase and yet inhibits the β-amylase of plants. The oxidised form of ascorbic acid inhibits α-amylase but is without action on β-amylase.

Willstätter and Rhodewald (Z. physiol. Chem. 1933, **221**, 13) find that of a variety of amylases some are, others are not inhibited by glycerol, whereas some do, others do not require the addition of phosphates. This they attribute to changes in the groupings in the molecule of the enzyme.

Amylase which has been rendered inactive by methods of precipitation can be re-activated by shaking with peptone or albumin solutions (Oparin and Kursanov, Biochem. Z. 1929, **209**, 181 ; 1932, **256**, 190). E. F. A.

AMYLENE, C_5H_{10}. The name is applied more particularly to the mixture of isomeric pentenes obtained by the dehydration of commercial amyl alcohol :

$$C_5H_{11}{\cdot}OH \rightarrow C_5H_{10} + H_2O$$

It is often applied, however, to the individual isomeric forms of pentene (*q.v.*).

Preparation.—A mixture of pentene hydrocarbons may be satisfactorily obtained from commercial amyl alcohol under the following conditions : Amyl alcohol (1·5 litres) and concentrated sulphuric acid (100 c.c.) are heated to vigorous boiling under a reflux condenser in which the water is maintained at such a temperature (60°–90°) as to allow a considerable amount of vapour to distil out of the apparatus ; the top of the condenser is connected with a second, efficiently cooled condenser, attached so as to permit downward distillation. The heating requires a maximum time of about eight hours. At first water and amyl alcohol pass over, whilst subsequently amylene distils. The distillate is washed with sodium hydroxide to remove sulphur dioxide and the amylene isolated by fractionation. The residue in the original flask contains amyl alcohol and *iso*amyl ether which are recovered by distillation with steam followed by fractionation. About 250 c.c. of amylene, 400 c.c. of *iso*amyl ether, and 500 c.c. of recovered amyl alcohol are obtained from 1,500 c.c. of the latter (Adams, Kamm, and Marvel, J. Amer. Chem. Soc. 1918, **40**, 1950)

Good yields of amylene hydrocarbon can be conveniently obtained by the pyrogenic-catalytic method using aluminium oxide as catalyst at temperatures between 350° and 550° (Ipatieff, Ber. 1903, **36**, 1990 ; Leendertse, Tulleners and Waterman, Rec. trav. chim. 1933, **52**. 515). An active catalyst is obtained by thinning commercial aluminium hydroxide to a paste with water and drying the latter at about 110° until a suitably coherent mass is obtained which can be broken into small pieces ; the pieces are placed in a furnace tube (4 cm. bore ; heated length, 60 cm.) and gradually heated in a stream of air to 450°, which temperature should be maintained for 1 hour. The alcohol is added drop by drop (165 grms. per hour) at the front end of the furnace tube and the vapours produced cooled first by ice and then by ice-salt. The crude hydrocarbon obtained at working temperatures in the neighbourhood of 350°–450° gives, after it has been dried with potash and rectified, over an 80% yield of pentene hydrocarbons.

Composition.—The amylene hydrocarbons obtained from commercial amyl alcohol consists essentially (probably entirely) of the three branched-chain pentenes (I–III),

$$CHMe_2{\cdot}CH : CH_2 \quad \text{(I)}$$

γ-Methyl-Δ^{α}-butene
(iso*Propylethylene*)

$$CMe_2 : CH{\cdot}CH_3 \quad \text{(II)}$$

β-Methyl-Δ^{β}-butene
(*Trimethylethylene*)

$$CH_2 : CMe{\cdot}CH_2{\cdot}CH_3 \quad \text{(III)}$$

β-Methyl-Δ^{α}-butene
(as-*Methylethylethylene*)

the proportion in which these are formed depending on the method of preparation and on the conditions of dehydration employed. By the foregoing method of preparation employing sulphuric acid as dehydrating agent the principal products are II and III, with but very little of I. It is to be borne in mind, however, that the branched-chain pentenes undergo polymerisation somewhat readily in presence of sulphuric acid, the rate of reaction depending largely on the concentration of the acid and the temperature, whilst the polymerising tendency of the individual hydrocarbons decreases in the order $CMe_2:CHMe$, $CMeEt:CH_2$, and $CHMe:CHEt$ (Norris and Joubert, J. Amer. Chem. Soc. 1927, **49**, 1873).

Properties.—As usually prepared, amylene is a colourless liquid, b.p. 28°–36° (*circa*) and sp.gr. 0·6873 (*circa*). It shows the chemical properties of its component olefins (*q.v.*). Under certain experimental conditions the components can undergo some degree of interconversion. At room temperature trimethylethylene and *as*-methylethylethylene dissolve in an equimolecular quantity of 61% sulphuric acid, the former hydrocarbon entering solution slightly the more readily ; but although acid of 61% strength is sufficient to convert these two hydrocarbons slowly into their dimerides, it is insufficient to attack *iso*propylethylene.

E. H. F.

AMYLOFORM. An antiseptic dressing prepared by the action of formaldehyde upon starch (Claassen, Pharm. Zeit. **41**, 625).

AMYLOSE, AMYLOPECTIN. Starch is composed of two different substances, one of which forms the envelope of the granule and the other the content. These have been named α- and β-amylose by Meyer, or amylopectin and amylose by Maquenne, who stated that starch is 15–20% amylopectin and 80 to 85% amylose. Their complete separation is difficult; amylopectin contains the phosphorus of starch.

According to Samec and Mayer (Kolloid-Beih. 1914, **6**, 23) amylose has $[\alpha]_D$ +189° and a mean molecular weight of 80,000, whereas amylopectin has $[\alpha]_D$ +195° and about 130,000 as its molecular magnitude.

Schardinger found that starch, when fermented by *Bacillus macerans*, gave rise to crystalline α- and β-dextrins, from which two series of polyamyloses have been isolated by Pringsheim. These are :

α-Series.

Diamylose, $(C_6H_{10}O_5)_2$ $[\alpha]_D$+136°.
Tetra-amylose, $[(C_6H_{10}O_5)_2]_2$ $[\alpha]_D$+148°.
α-Hexa-amylose, $[(C_6H_{10}O_5)_2]_3$ $[\alpha]_D$+139°.

β-Series.

Triamylose, $(C_6H_{10}O_5)_3$ $[\alpha]_D$+151°.
β-Hexa-amylose, $[(C_6H_{10}O_5)_3]_2$ $[\alpha]_D$+158°.

The β-series is derived from amylopectin.

These polyamyloses form halogen addition products, esters, and ethers (Pringsheim, Ber. 1912, **45**, 2533 ; 1916, **49**, 364 ; 1922, **55** [B], 1428, 1443, 1446 ; 1926, **59** [B], 2058 ; 1927, **60** [B], 1709).

The constitution of these polyamyloses has not as yet been definitely explained ; both series are converted into a maltose derivative by means of acetyl bromide. In them two or three molecules combine with the loss of two or three molecules of water : they are indifferent to Fehling's solution.

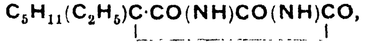
The methylation method of Haworth indicates a chain length of 25–30 α-glucoso-pyranose residues for methylated starch of various origins or prepared in a variety of ways. He likewise finds amylopectin to be of greater molecular size than amylose, but considers the chemical unit of starch is of limited size with a molecular weight around 5,000, such units undergoing aggregation to physical units of much larger dimensions. He has prepared a derivative of starch undegraded in the chemical sense (Baird, Haworth, and Hirst, J.C.S. 1935, 1200). The breakdown units of starch investigated by Haworth having chains of 17, 12, 9, 7, and 5 glucose units have all a terminated chain of α-glucose units (Haworth and Machemer, J.C.S. 1932, 2270 ; Hirst, Plant and Wilkinson, *ibid.* 2375). The same applies to dextrins prepared by heating starch with glycerol having a chain of 8 and 12 glucose residues ; they give a deep red colour with iodine (Haworth, Hirst, and Plant, J.C.S. 1935, 1214). E. F. A.

***tri-iso*-AMYLSTIBINE** *v.* ANTIMONIALS, ORGANIC.

***tri-n*-AMYLSTIBINE** *v.* ANTIMONIALS, ORGANIC.

α- AND β-AMYRINS. These isomeric monohydric triterpene alcohols, $C_{30}H_{50}O$, are most conveniently isolated from Manila elemi (Vesterberg, Annalen, 1922, **428**, 242). *α-Amyrin*, m.p. 180°–181·5°, $[\alpha]_D$ +91·5°, and *β-amyrin*, m.p. 193°–194°, $[\alpha]_D$ +99·8°, are both characterised by a series of crystalline esters and on oxidation give the corresponding ketones, *α-amyrone*, m.p. 125°–126°, and *β-amyrone*, m.p. 178°–180° (Vesterberg, Ber. 1891, **24**, 3834). From the nature of the products obtained by dehydrogenation with selenium it is clear that the amyrins are derivatives of hydropicene (Ruzicka, Brüngger, Egli, Ehmann, Furter, and Hösli, Helv. Chim. Acta, 1932, **15**, 431). F. S. S.

AMYTAL. 5-Ethyl-5-*iso*amyl-barbituric acid. Ethyl*iso*amylmalonyl urea,



$$C_5H_{11}(C_2H_5)C{\cdot}CO(NH)CO(NH)CO,$$

m.p. 153°–155°. Sedative and hypnotic, resembling barbital in its effect.

ANABASINE, $C_{10}H_{14}N_2$, b.p. 276°, 104°–105°/2 mm., $[\alpha]_D^{20}$ −82·2°, is 3-pyridyl-2′-piperidine. It is the chief alkaloid of *Anabasis aphylla* L., N.O. Chenopodiaceæ, in which it is accompanied by lupinine and aphylline (the latter related to sparteine). This steppe-plant of Central Asia contains over 2% of alkaloid, which is now extracted on the spot on a large scale and used as insecticide. Anabasine is isomeric with nicotine and has almost the same toxicity (Orechoff and Menschikoff, Ber. 1931, **64** [B], 266 ; 1932, **65** [B], 232). G. B.

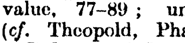
ANACARDIUM NUT (*Cashew nut, Kajoo*) is the seed of *Anacardium occidentale* Linn., a tree which is indigenous to Brazil, Central America, and the West Indies, but has been transplanted and naturalised in many parts of India. The drupaceous fruit rests on a fleshy peduncle, from which a spirit is distilled in Mozambique and in Western India. The mesocarp (inner part of the rind) contains a corrosive oily juice, containing "cardol" and "anacardic acid" (P. P. Pillay, J. Indian Chem. Soc. 1935, **12**, 226) and resins (*cf.* Städeler, Annalen, 1847, **63**, 137; Ruhemann and Skinner, J.C.S. 1887, **51**, 663; Spiegel and Dokrin, Ber. 1896, **5**, 309; Joseph and Sudborough, J. Indian Inst. Sci. 1923, **5** [x], 152), which has an inflammatory and blistering action on the human skin. This juice darkens on exposure to the air, giving a permanent dark brown (not black) stain on linen; no definite statements appear to have been made, however, concerning its possible use as a marking ink, as is the case with the analogous liquid obtained from the allied Marking-Nut of India (*q.v.*). The juice which is rendered from the rind by heating the nuts is used at Goa for tarring boats and preserving wood against attack by insects, etc. (*cf.* Dymock, Pharm. J. 1877 [iii], **7**, 730), and within the last five years a number of patents have appeared in the name of the Harvel Corporation for the preparation of varnish-like compositions from this "cashew nut shell liquid" (*cf.* B.P. 175574, 452413; U.S.P. 1838072–3, 1838077, 1950085, etc.). According to U.S.P. 1777808 (Franklin Baker Co.) the shell oil is rendered by plunging the nuts in a bath of molten solder.

The native method of setting fire to piled heaps of the fruits in order to crack the shells and facilitate the separation of the edible kernels has also been adopted by commercial organisations. The cashew kernel contains about 38–48% of a pleasant bland oil, resembling almond oil in flavour; the oil, however, is unimportant as a commercial article, since the kernels ("nuts"), which are eaten raw or partly roasted, command a high price as a confectionery nut.

The following characteristics have been recorded for samples of cashew kernel oils: n^{40} 1·461–1·4632; saponification value, 182–197; iodine value, 77–89; unsaponifiable matter 0·6% (*cf.* Theopold, Pharm. Zentr. 1908, **49**, 1057; Bolton and Jesson, Analyst, 1915, **40**, 3; Georgi, Malay Agric. J. 1922, **10**, 301; Gobert, Ann. Falsif. 1931, **24**, 260; West and Cruz, J. Phil. Sci. 1923, **23**, 337). According to Patel, Sudborough, and Watson (J. Indian Inst. Sci. 1923, **6**, 111) the fatty acids of a sample of the oil consisted of:—oleic acid, 74%; linolic acid, 7·7%; palmitic acid, 6·4%; stearic acid, 11·0%; lignoceric acid, 0·5%.

E. L.

ANÆSTHESINE. Trade name for ethyl *p*-aminobenzoate,



m.p. 90°–91°. Local anæsthetic.

ANÆSTHETICS. Drugs which cause loss of sensation, and hence permit the painless performance of surgical operations, may be broadly divided into two groups according as they produce loss of consciousness by their action on the higher centres of the brain or local insensibility to pain in the area to be operated upon. The members of these two groups are termed respectively *general anæsthetics* and *local anæsthetics*.

General Anæsthetics. The substances employed for the production of anæsthesia are general cell poisons. When, however, they are administered in limited quantity to the higher living organisms they exert a selective action on the centres of the brain concerned with consciousness and on the central nervous system in general, but do not appreciably affect those nervous centres which control respiration and the circulation. The mechanism by which they exert their action is unknown. Since, however, they are relatively inert chemically, undergo little, if any, change in the organism and are largely excreted in an unchanged form, this mechanism is presumably physical in nature, and many attempts have, in fact, been made to correlate certain of their physical properties, such as their partition coefficients between oil and water, their surface activities and their adsorbabilities, with their anæsthetic activities. None of these attempts has been wholly successful. It is nevertheless probable that both their solubilities in fats or lipoids and their adsorbabilities play some part in determining the magnitude of their activities.

While there is a large number of substances, particularly amongst the hydrocarbons, ethers and esters, which are capable of producing anæsthesia in the higher living organisms, few are actually used in practice. In some instances this may be due to the failure to recognise the suitability of a particular compound for the purpose in question. Usually, however, it is because the substances do not sufficiently conform to one or other of the various criteria which an anæsthetic must satisfy before it can be utilised in surgical practice. An ideal anæsthetic should (1) be capable of easy administration, (2) induce anæsthesia without pain or discomfort, (3) cause a cessation of all voluntary and many reflex movements, (4) produce a sufficient relaxation of the muscles for the needs of the surgeon, (5) be capable of control by the anæsthetist so that the depth of the anæsthesia can be rapidly increased or decreased at will, (6) have little or no influence in the quantity used upon the respiration and the circulation, and (7) be naturally and rapidly eliminated from the system after completion of the operation. No known anæsthetic conforms completely to this ideal, and it is for this reason that the examination of possible new drugs of this type continues.

Several routes are available for the administration of an anæsthetic. If it is a gas or a readily volatile liquid, it may be inhaled into the lungs, and this is, in fact, the method of administration usually employed in practice. Anæsthesia may, however, be induced by the introduction of the anæsthetic, if necessary suitably diluted, into the rectum, or by its injection directly into the blood stream. Whichever method is adopted the drug rapidly passes into the blood, by which it is conveyed to the brain and other parts of the organism. The rectal and injection methods suffer from the disadvantage that the resulting anæsthesia is not under the control of the administrator. With the inhalational method, on the other hand, in which it is necessary, except for operations of very short duration, to administer the anæsthetic continuously during the period for which it is desired to maintain anæsthesia, the depth of the latter can be rapidly increased or diminished by varying the rate of administration of the anæsthetic. Two principal methods are employed in the administration of inhalational anæsthetics: either one or other of the various types of inhalers which have been devised is used; or the so-called "open" method, in which the liquid anæsthetic is allowed to drop at a suitable rate on to a mask or piece of lint or other material placed loosely over the patient's face; this method is obviously inapplicable to gaseous anæsthetics.

The anæsthetics in common use are nitrous oxide, ethyl chloride, ether, and chloroform. In recent years more or less success has also been obtained with acetylene, ethylene, *cyclo*propane and divinyl ether, but the suitability of these substances cannot yet be regarded as established.

Nitrous oxide (Laughing gas).—This gas should be free from the higher oxides of nitrogen, which are toxic substances. Moisture should also be absent, since, if present in appreciable amount, it tends to freeze in the valves of the cylinder from which the gas is released. Anæsthesia of sufficient duration for short operations, such as extraction of teeth, is produced by breathing the pure gas from an inhaler. For longer operations the anæsthesia must be maintained by the continuous administration of the gas, in which case asphyxiation must be prevented by the simultaneous or intermittent administration of oxygen or air. Nitrous oxide is one of the safest anæsthetics, but it hardly produces sufficient relaxation of the muscles for major operations. For this reason it is sometimes used in combination with ether.

Ethyl chloride is supplied by the manufacturers in pure form condensed to a liquid in glass tubes fitted with metal valves. Some preparations contain about 0·5% of eau de Cologne, which is added in order to disguise its odour. It may be administered either by the open method or by means of an inhaler. The use of ethyl chloride alone is restricted to short operations. It possesses the advantage that the period of induction is very short and, for this reason, it is sometimes employed as a preliminary to ether anæsthesia.

Ether.—Anæsthetic ether has a specific gravity of 0·720 and is described as "Ether Pure 0·720" or "Ether Meth. Purif. 0·720" (alternatively, "methylated ether") according as it is prepared from pure ethyl alcohol or from methylated spirit. It must be free from the toxic peroxides and aldehyde which are formed from it when it is exposed to heat and light. According to F. W. Nitardy and M. W. Tapley (J. Amer. Pharm. Assoc. 1928, **17**, 966) the formation of these impurities is inhibited if the ether is stored in contact with an adequate surface of metallic copper or of copper salts. Ether may be administered by means of an inhaler or by the open method. Owing to its irritating action on mucous membranes, particularly of the respiratory passages, induction is sometimes commenced with nitrous oxide or ethyl chloride. About 18% of ether in inspired air is necessary to induce anæsthesia, but smaller percentages are required to maintain it.

Two methods have been used for the rectal administration of ether. In one of these the vapour is introduced directly into the rectum. In the other a solution of ether in olive oil or paraffin to which a narcotic such as paraldehyde or chloretone has been added, is used. Anæsthesia may also be produced by the intravenous injection of a 5% solution of ether in saline; this method is, however, rarely used.

Chloroform.—In the presence of air, and when exposed to light, chloroform undergoes oxidation to phosgene and hydrogen chloride, both of which are toxic. It is therefore usual for manufacturers to add to anæsthetic chloroform 1–2% of alcohol, which inhibits this change, and to supply the liquid in amber-coloured bottles. Chloroform can be administered either by the open method or by means of an inhaler. The former method is the simpler, but the latter possesses the advantage that it enables the drug to be administered in conjunction with another anæsthetic such as nitrous oxide. Of the common anæsthetics, chloroform produces the most satisfactory anæsthesia from the viewpoint of the surgeon. Nevertheless, its use is associated with most risk to the patient. There is therefore a tendency to avoid employing it unless other factors make the use of ether undesirable. For the production of anæsthesia inhaled air must contain from 2 to 3% of chloroform, but smaller concentrations suffice for its maintenance.

Other anæsthetics.—Of the anæsthetics of recent introduction three, acetylene, ethylene and *cyclo*propane, are gases and hence can be administered by methods similar to those used with nitrous oxide. The use of *cyclo*propane has scarcely passed beyond the stage of animal experimentation; commercial preparations of the substance are, however, available. Acetylene and ethylene are similar in their action and possess the great advantage over other anæsthetics that anæsthesia is induced with ease while recovery rapidly follows the cessation of their administration. With ethylene rather more, and with acetylene considerably more, oxygen can be administered than with nitrous oxide. Ethylene has been used extensively in America (A. B. Luckhardt, J. Amer. Med. Assoc. 1924, **83**, 2060), where it is claimed that, in addition to the advantages mentioned above, it has little or no effect on the pulse, blood pressure, or kidney. It produces greater muscular relaxation than does nitrous oxide, but this is insufficient for abdominal operations; for the latter purpose it is sometimes employed in conjunction with ether. Commercial acetylene usually contains poisonous impurities such as phosphine, which render it unsuitable for anæsthetic purposes. The purified product, which is known in Germany as *narcylen*, has, however, been successfully used in a number of operations (C. J. Gauss and H. Wieland, Klin. Woch. 1923, **2**, 113, 158). Satisfactory results have also been obtained with it in this country (F. E. Shipway, Lancet, 1925, I, 1126), but two difficulties were encountered: the objectionable odour even of the purified gas, and the absence of a simple method for freeing it from acetone, which is necessarily present in the cylinders in which it is compressed. Both ethylene and acetylene suffer from the disadvantage of forming explosive mixtures with oxygen and in a few cases explosions have occurred during their use as anæsthetics. With adequate precautions, however, it is doubtful if the risks attending their use are much, if any, greater than with ether. Divinyl ether for anæsthetic purposes has been marketed by one firm under the trade name of *vinethene*. Its use as an anæsthetic has been advocated by C. D. Leake, P. K. Knoefel, and A. E. Geudal (J. Pharm. Exp. Ther. 1933, **47**, 5) as a result of observations on animals. It has recently been employed in America for the production of surgical anæsthesia.

Pre-anæsthetic medication.—With the object of diminishing the secretion of saliva and mucus and of lessening the apprehension of the patient, it has long been the custom to give injections of atropine, morphine, or hyoscine as a preliminary to the administration of an anæsthetic. In recent years such pre-anæsthetic medication, or pre-medication as it is frequently termed, has been considerably extended and it is now rapidly becoming the practice to produce anæsthesia by the combined action of a non-volatile narcotic with a volatile or gaseous anæsthetic. In this method the non-volatile narcotic, which is termed a basal narcotic, is used to render the patient unconscious before the administration of the anæsthetic, which then takes place in the customary manner. Such a procedure possesses many advantages. Not only does it lessen the fear of the patient, but it enables surgical anæsthesia to be produced with a smaller amount of anæsthetic than would be necessary in the absence of the narcotic, thus diminishing the unpleasant effects which certain of the former produce. It renders possible, moreover, the use of nitrous oxide, the safest and least unpleasant of the common anæsthetics, in operations for which this gas would not alone produce anæsthesia of a sufficient depth. The administration of basal narcotics can be made orally, per rectum, or by intravenous or intramuscular injection, according to the nature of the narcotic employed. The following are the more important basal narcotics :

Paraldehyde.—This is usually administered rectally as a 10% solution in normal saline.

Avertin (tribromoethyl alcohol) is given per rectum in 3% aqueous solution. Care must be exercised in the preparation of the solution, since avertin is decomposed by heat into hydrogen bromide and dibromoacetaldehyde, which have an irritant action on the rectum. In view of this difficulty, avertin is supplied by the makers in the form of a solution, known as averatin fluid, in amylene hydrate, 1 c.c. of which contains 1 grm. of the solid. Avertin has been employed alone as a general anæsthetic. This, however, necessitates the administration of larger doses, which it is not now considered desirable to employ.

Amytal (sodium ethyl-*iso*amyl-barbiturate) is given hypodermically.

Pernocton (sodium *sec*butyl-β-bromoallyl-barbiturate) is injected intravenously.

Nembutal (sodium ethyl-α-methylbutyl-barbiturate) is suitable either for oral administration or intravenous injection.

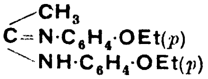
Evipan (*N*-methyl-CC-*cyclo*hexenylmethyl-barbituric acid) can be administered orally as an hypnotic (Anæsthetic Committee of the Medical Research Council, Lancet, 1933, **135**, ii, 18), or injected intravenously as a basal narcotic or general anæsthetic (R. Jarman, Brit. Med. J. 1934, I, 796). Its action is evanescent. Like many barbiturates, evipan-sodium decomposes fairly rapidly in aqueous solution.

Local Anæsthetics.—Local insensibility to pain for surgical purposes can be produced by freezing the tissue in the area concerned or by the use of certain drugs which are known as local anæsthetics. Freezing is effected by the rapid evaporation of either ethyl chloride or ether, a fine spray of which is caused to impinge on the skin. This method is, however, of limited applicability and is obviously unsuited to any but minor and superficial operations. Local anæsthetics are administered in a variety of ways. In *surface anæsthesia* they are applied directly to a mucous surface, such as that of the eye, which they penetrate and anæsthetise ; in *infiltration anæsthesia* they are injected directly into the tissue to be operated upon, where they paralyse the sensory nerve endings ; while in *regional anæsthesia* they are injected around, or into, the nerve trunk supplying the sensory nerves in the tissue concerned and thus create a block in the path of these nerves at a point distant from the field of operation. Allied to these methods is that of *spinal anæsthesia*, in which the insensibility to pain extends over the whole of the lower part of the body from about the diaphragm downwards. Spinal anæsthesia is produced by the injection by lumbar puncture of certain drugs of the local anæsthetic group into the subarachnoid space of the vertebral canal, where they mix with the cerebrospinal fluid and paralyse both sensory and motor nerves at their junctions with the spinal cord. Owing to the more extensive anæsthesia produced, this method is not usually regarded as one of local anæsthesia, although it resembles the latter in leaving the consciousness of the patient unaffected. Local anæsthetics are usually administered in the form of a solution in physiological saline. In view of the toxic effects which they produce when they rapidly enter the circulation, it is customary, in infiltration and regional anæsthesia, to add a suitable quantity of adrenaline to the solution. This causes a constriction of the small blood vessels in the region of the injection and hence prevents the rapid dispersal of the local anæsthetic throughout the system.

Many drugs are available for use as local anæsthetics. Cocaine was originally the sole representative of this group. When, however, it was recognised that the local anæsthetic properties of the alkaloid were associated with a particular group in its structural formula, the possibility of synthesising a large number of potential local anæsthetics arose, a possibility which has by no means been neglected in the past and which still continues to receive attention. Cocaine is the benzoic ester of an aminoalcohol (methylecgonine), and it is to this fact that its local anæsthetic properties must be ascribed, although the structure of the rest of the molecule is not without influence on its activity. Corresponding with the above relationship, many benzoic and aminobenzoic esters of other and simpler aminoalcohols behave to varying degrees as local anæsthetics, but few are considered suitable for use in practice. The following are the more important naturally occurring and synthetic representatives of this group: *cocaine* (methyl benzoyl ecgonine); *tropacocaine* (benzoyl-ψ-tropine); *psicaine* (*d*-ψ-cocaine); *novocaine* or *procaine* (diethylaminoethyl *p*-aminobenzoate); *stovaine* (dimethylaminomethyl methyl ethyl carbinyl benzoate); *β-eucaine* (2 : 2 : 6-trimethyl-4-benzoyloxypiperidine); *alypine* (tetramethyldiaminodimethyl ethyl carbinyl benzoate); *neothesin* (γ-2-methylpiperidinopropyl benzoate); *isocaine* (di*iso*propylaminoethyl *p*-aminobenzoate); *butyn* (γ-di-*n*-butylaminopropyl *p*-aminobenzoate); *tutocaine* (αβ-dimethyl-γ-dimethylaminopropyl *p*-aminobenzoate); *larocaine* (ββ-dimethyl-γ-diethylaminopropyl *p*-aminobenzoate); *panthesine* (β-diethylamino-δ-methylamyl *p*-aminobenzoate); *pantocaine* (dimethylaminoethyl-*p*-*n*-butyl aminobenzoate); *apothesine* (γ-diethylaminopropyl cinnamate). Because of the necessity of dissolving them in water, these anæsthetics are employed in the form of salts. Nevertheless, the free base is the active agent, as is shown by the fact that acidity diminishes and alkalinity increases the potency of this type of anæsthetic whereas that of a non-basic anæsthetic, such as benzyl alcohol, is uninfluenced by changes in the p_H of the solution. Any influence tending to increase the hydrolytic dissociation of anæsthetics of the former kind as, for example, by employing them in the form of salts with weak acids, should therefore increase their anæsthetic activities. This has led to the introduction into medicine of the *borocaines* (A. J. Copeland and H. E. F. Notton, Brit. Med. J. 1925, ii, 547), which are the borates of the common local anæsthetics. It is claimed that the borocaines are more potent as surface anæsthetics than the corresponding hydrochlorides.

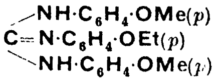
Another group of local anæsthetics consists of alkyl esters of substituted benzoic acids. These resemble the members of the above group in containing both an ester and a basic grouping; the latter, however, is present only in the acidic moiety of the molecule. Examples are: *anesthesine* (ethyl *p*-aminobenzoate); *propaesine* (propyl *p*-aminobenzoate); *scuroform* (*n*-butyl *p*-aminobenzoate); *cycloform* (*iso*-butyl *p*-aminobenzoate); *orthoform* (old: methyl *p*-amino-*m*-hydroxybenzoate; new: methyl *m*-amino-*p*-hydroxybenzoate); *nirvanine* (methyl *p*-diethylglycylamino-*m*-hydroxybenzoate). The salts of most of these compounds undergo considerable hydrolytic dissociation when dissolved in water. They are therefore only used as the free base in powder form; as such they are incorporated in ointments for the relief of burns, etc.

Despite the relationship between chemical constitution and local anæsthetic action which is apparent in the two groups of compounds mentioned above, other substances of quite different structure are occasionally discovered which possess marked local anæsthetic properties. This is illustrated by the two compounds *holocaine*,



$$C\begin{cases}CH_3\\ =N{\cdot}C_6H_4{\cdot}OEt(p)\\ NH{\cdot}C_6H_4{\cdot}OEt(p)\end{cases}$$

and *acoine*,



$$C\begin{cases}NH{\cdot}C_6H_4{\cdot}OMe(p)\\ =N{\cdot}C_6H_4{\cdot}OEt(p)\\ NH{\cdot}C_6H_4{\cdot}OMe(p)\end{cases}$$

But the most important local anæsthetic of a type unrelated to the above groups is, at the present time, undoubtedly the substance known in this country as *percaine* and in America as *nupercaine*. Percaine is the β-diethylaminoethylamide of 2-butoxyquinoline-4-carboxylic acid. Its anæsthetic potency is much greater than that of cocaine, although it is also more toxic.

Many of the above local anæsthetics do not, for various reasons, find much application at the present time. Thus, cocaine is not only very toxic but certain individuals exhibit an idiosyncrasy towards it. It is, moreover, unstable in solution and cannot be sterilised by heat. It has therefore largely fallen into disuse for most purposes, although it is still retained as a surface anæsthetic. Novocaine, on the other hand, is much less toxic, and its solutions can be sterilised by heat. It suffers, however, from the disadvantage that it will not diffuse rapidly through mucous membranes. Novocaine is thus useless for the production of surface anæsthesia, but it has been used widely for all other types and is the anæsthetic agent present in certain preparations (*spinocaine*, *gravocaine*, and *durocaine*) which are employed for the production of spinal anæsthesia. Stovaine is unsuitable for infiltration anæsthesia owing to its irritant action on tissues, but it has found considerable use as a spinal anæsthetic. There is a tendency, however, for all of these common anæsthetics to be displaced by percaine. In the form of its hydrochloride, this drug is stable in solution and such solutions can, in the complete absence of alkali, be sterilised by boiling without the occurrence of decomposition. It is a remarkably potent drug, possessing an activity which is about 40 times that of novocaine, while its toxicity is only 25 times that of the latter. It has proved to be very successful as a spinal anæsthetic and can also be used for infiltration and surface anæsthesia. E. S.

ANAGYRINE. Amorphous alkaloid, $C_{15}H_{20}ON_2$, $[\alpha]_D^{20}$ −165·3, from *Anagyris foetida* (H. R. Ing, J.C.S. 1933, 504, A, 727) (*v.* Sparteine).

ANALGEN. Trade name for ethoxylbenzoylaminoquinoline,

$$C_9H_5N(OC_2H_5)(NH{\cdot}CO{\cdot}C_6H_5),$$

formerly manufactured as an antisyphilitic.

ANALGESINE. *Antipyrine.* Phenyldimethylpyrazolone (*v.* Pyrazole).

ANALUTOS. *Kalmopyrin.* Calcium acetylsalicylate.

ANAMIRTA PANICULATA (Fam. Menispermaceæ). Cocculus Indicus. The drug, the dried fruit of an East Indian shrub, contains the poisonous picrotoxin, $C_{30}H_{34}O_{13}$, as well as anamirtin, $C_{19}H_{24}O_{10}$, and cocculin, $C_{19}H_{26}O_{10}$ (*v.* PICROTOXIN). It has been used for poisoning fish. In medicine it has had a limited use for destroying skin parasites.

ANANDONIS GREEN. Hydrated chromium sesquioxide (*v.* CHROMIUM).

ANATASE or *Octahedrite.* One of the trimorphous forms of titanium dioxide (TiO_2) met with as crystallised minerals, the others being rutile and brookite. It is found as small, isolated crystals of a steel-blue or honey-yellow colour, in schistose rocks, particularly in the Alps; and as microscopic crystals is of common occurrence in sedimentary rocks.
L. J. S.

ANAYODIN. Iodoxy-quinoline sulphonic acid. Amœbacide.

ANCHUSA *v.* ALKANET.

ANCYLITE. A hydrated basic carbonate of cerium, lanthanum, and didymium and strontium, $4Ce(OH)CO_3{\cdot}3SrCO_3{\cdot}3H_2O$, found as small, yellow, orthorhombic pyramids with curved faces in syenite-pegmatite at Narsarsuk in the Julianehaab district, south Greenland; sp.gr. 3·95.

An allied mineral, with the formula

$$4(Ce,La,Di)_2(CO_3)_3{\cdot}5SrCO_3{\cdot}(Ce,La,Di)_2O_3$$

has been found as orthorhombic grains forming, with celestine, monazite, felspar, etc., a constituent of crystalline limestone at Ambatoarina in Madagascar. This has been named ambatoarinite (A. Lacroix, 1916). L. J. S.

ANDALUSITE. One of the three modifications of crystallised aluminium silicate, Al_2SiO_5, and belonging to the orthorhombic system; the other modifications being the minerals kyanite and fibrolite. Andalusite occurs in crystalline schists and metamorphic rocks, the variety *chiastolite* being specially abundant in the baked clay-slates surrounding intrusive igneous masses. It is also found as small crystals and grains in some granites, due probably to fragments of the surrounding slates having been incorporated in the igneous magma. Grains of andalusite are found in the sands and sedimentary rocks derived from these primary rocks. The pleochroism, from olive-green to rose-red, is a characteristic feature of the mineral under the microscope. D 3·18, H 7½. Large, rough, opaque crystals are well known from Lisens-Alp in the Tyrol. Clear transparent pebbles of a rich brown colour are found in the Rio Jequitinhonha in Minas Geraes, Brazil; this material when cut as a gem-stone displays the strong pleochroism. The variety known as chiastolite shows in cross-sections of the prismatic crystals a dark cross of carbonaceous material enclosed in the lighter coloured andalusite; such material is cut as a gem-stone or charm. Large crystals of chiastolite have been found in considerable numbers at Bimbowrie, near Olary in South Australia.

More recently andalusite has been mined on White Mountain, Mono Co., California, and with *dumortierite* in Nevada and Arizona, as a refractory material and for the manufacture of the porcelain cores of sparking plugs (A. B. Peck, Amer. Min. 1924, **9**, 51; P. F. Kerr, Econ. Geol. 1932, **27**, 614). It has also been found as large blocks in the Ninghanboun Hills in the South-Western Division of Western Australia (E. S. Simpson, J. Roy. Soc. West. Australia, 1931, **17**, 138; 1932, **18**, 75).
L. J. S.

ANDAQUIES WAX *v.* WAXES.

ANDESINE. A soda-lime felspar belonging to the group of plagioclase-felspars (*v.* FELSPAR).
L. J. S.

ANDESITE. A group of volcanic rocks of intermediate composition, containing on an average 60% of silica, and corresponding to the plutonic diorites. They are usually dark-coloured, compact rocks, sometimes with a porphyritic structure or a vesicular texture; and are composed essentially of plagioclase-felspar with a ferromagnesian mineral, and sometimes a glassy base. According to the ferromagnesium mineral present, the varieties hornblende-andesite, biotite-andesite, and pyroxene-andesite are distinguished. When quartz is present the rock grades into the dacites. Sp.gr. 2·6–2·8. They are of wide distribution. The Andes of South America and the Cordilleras of Central and North America are built up largely of andesites; and here, as well as in Hungary, ore-deposits, particularly those of gold and silver, frequently occur in connection with them. In the British Isles they are abundant in the Midland Valley of Scotland, the Cheviot Hills, the Lake District, and in North Wales, and in these districts are quarried for road-stones. On the Continent they are also used for building stone and millstones. L. J. S.

ANDORITE. Sulphantimonite of silver and lead, $AgPbSb_3S_6$, crystallising in the orthorhombic system. The mineral was independently described in 1892 from Felsőbánya in Hungary and Oruro in Bolivia under the names andorite, *sundtite,* and *webnerite.* It is dark steel-grey with metallic lustre, and a shining black streak; no cleavage; sp.gr. 5·35; H 3¼. Analyses show 10–11·7% of silver (according to the formula $Ag{=}12{\cdot}42\%$), there being small amounts of copper also present. At Oruro, in the San José and Itos Atocha mines, it occurs rather plentifully as well-formed crystals and as a massive silver ore (Prior and Spencer, Min. Mag. 1897, **11**, 286; Spencer, *ibid.* 1907, **14**, 316). L. J. S.

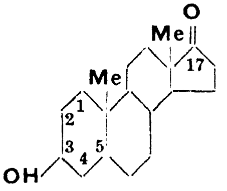
ANDROPOGON OILS *v.* OILS, ESSENTIAL.

ANDROSIN, glycoside of acetovanillone.

$$C_6H_{11}O_5{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CH_3$$

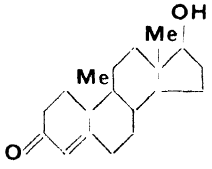
is obtained from the rhizome of *Apocynum androsemifolium* (Moore, J.C.S. 1909, **95**, 734).
E. F. A.

ANDROSTERONE, *Androstane*-3-*ol*-17-*one*, is a saturated hydroxyketone, $C_{19}H_{30}O_2$, m.p. 182°–183° (corr.), $[\alpha]_D$ +94° in alcohol, which has been isolated in minute amount from male urine by A. Butenandt (Naturwiss. 1933, **21**, 54; A. Butenandt and K. Tscherning, Z. Physiol. Chem. 1934, **229**, 167, 185) and which possesses the physiological action of a male sex hormone. The same ketone has also been obtained by the vigorous oxidation of *epi*-cholestanyl acetate, followed by hydrolysis, and its constitution definitely established :



(L. Ruzicka, M. W. Goldberg, J. Meyer, H. Brüngger, and E. Eichenberger, Helv. Chim. Acta, 1934, **17**, 1395). *See* Hormones.

$\Delta^{4:5}$-*Androstene-3-one-17-ol, Testosterone*, is an unsaturated hydroxyketone, $C_{19}H_{28}O_2$, m.p. 154·5°–155·5°, $[\alpha]_D$ +109° in alcohol, which has been isolated in very small amount from the testes of bulls (E. Laqueur, K. David, E. Dingemanse, and J. Freud, Acta brevia Neerl. 1935, **5**, 84 ; K. David, *ibid.* 85, 108), and which possesses a powerful activity as a male sex hormone. Its structure has been established with certainty by its preparation from cholesterol (L. Ruzicka and A. Wettstein, Helv. Chim. Acta, 1935, **18**, 1264).

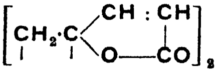


See Hormones. G. A. R. K.

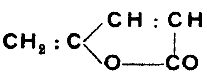
ANEMOLIC ACID, CONSTITUTION OF (Y. Asahina and A. Fujita, J.C.S. 1920, A, i, 70). Anemonin reduced in AcOH with NaHg gives *dihydroanemonin*, $C_{10}H_{10}O_4$, m.p. 172°; this heated with HCl yields *anemolic acid*, $C_{10}H_{14}O_6$, considered to be identical with dilævulinic acid.

ANEMONE PULSATILLA. *Pasque Flower* (Fam. Ranunculaceæ). The irritant essential oil from this herb contains crystalline anemone camphor which slowly decomposes into anemonin and *iso*anemonic acid (B.P.C., 1934, 859). A similar or identical substance is contained in the vesicant essential oils of other species of Ranunculaceæ.

ANEMONIN, m.p. 158°, obtained from the vesicant essential oil of *Ranunculus scleratus*, was synthesised by Y. Asahina (J.C.S. 1920, A, i, 493), whence the formula



It is the dimeric product of protoanemonin,



of which the oil mainly consists.

ANEMONINIC ACID. Anemonin, $C_{10}H_8O_4$, on hydrolysis yields *a*-anemoninic acid, $C_{10}H_{12}O_6$, m.p. 116°; the β-isomeride, m.p. 210° (Asahina, J.C.S. 1916, A, i, 402). For synthesis, *see* Fujita (*ibid.* 1923, i, 535).

ANESIN *v.* Aneson.

ANESON. *Anesin. Chloretone. Chlorbutol.* Trade names for acetonechloroform, trichloro-*tert*-butyl alcohol, $(CH_3)_2C(CCl_3)OH$, m.p. 96° when anhydrous; the commercial product contains varying amounts of water. Sedative.

ANESTHESINE (ethyl *p*-aminobenzoate) *v.* Anæsthetics.

ANETHOLE, *p*-propenylanisole,

$$\cdot CHMe : CH \cdot C_6H_4 \cdot OMe$$

(*v.* Oils, Essential).

ANETHUM GRAVEOLENS. Oleum anethi, oil of dill (*v.* Oils, Essential).

ANEURIN. The name suggested by Jansen (1935) for pure *vitamin* B_1 (*q.v.*), which was first isolated in the crystalline form by Jansen and Donath (Chem. Weekblad, 1926, **23**, 201) (*v.* Vitamins). L. J. H.

ANGELICA, ESSENTIAL OIL OF. The oil distilled from the fresh root and from the fruit of *Archangelica officinalis*, Hook (N.O. Umbelliferæ). It is cultivated in France, Belgium, Italy, Thuringia and Saxony, and is found also in Northern Europe and Siberia. The yield of oil from the root is 0·15 to 0·40%, whilst the fruits yield 0·7 to 1%. The characteristics are: sp.gr. 0·857–0·918, opt. rot. +11 to +32. Contains phellandrene, valeric acid, hydroxymyristic acid, hydroxypentadecylic acid, and a crystalline lactone. Angelica oil is used in the preparation of liqueurs, chiefly Chartreuse and Vulneraire. C. T. B.

ANGELINE, $C_{10}H_{13}O_3N$ (*surinamine, rhatanine*), m.p. above 233° (Hiller-Bombien, Arch. Pharm. 1892, **230**, 513 ; Goldschmiedt, Monatsh. 1913, **33**, 1379 ; **34**, 659), is identical with *l*-*N*-methyltyrosine (*v.* Tyrosine) (*cf. also* Winterstein, Z. physiol. Chem. 1919, **105**, 20). It has been synthesised in various ways (Johnson and Nicolet, Amer. Chem. J. 1912, **47**, 459 ; Fischer and Lipschitz, Ber. 1915, **48**, 360 ; Kanevskaja, J. pr. Chem. 1929 [ii], **124**, 48).

ANGLESITE. Native lead sulphate ($PbSO_4$), forming brilliant, colourless, orthorhombic crystals, isomorphous with baryte ($BaSO_4$) and celestine ($SrSO_4$). It occurs in the upper oxidised zones of veins of lead ore, having resulted by the alteration of galena (PbS). It is less common than cerussite ($PbCO_3$), with which it has sometimes been mined as an ore of lead. Good crystals have been found at many localities, *e.g.* Monteponi in Sardinia, Broken Hill in New South Wales, Tsumeb in South-West Africa, etc. The mineral takes its name from the Isle of Anglesey, where crystals were found by W. Withering, in 1783, in the Parys copper mine. L. J. S.

ANGLOPYRIN *v.* Aspirin.

ANGOSTURA BARK or **ANGUSTURA BARK** *v.* Cusparia Bark.

ANGOSTURIN *v.* Cusparia Bark.

ANHALAMINE *v.* Isoquinoline Alkaloids (Cactus).

ANHALINE=hordenine, *q.v.*

ANHALMINE, ANHALONIDINE, ANHALONINE *v.* ISOQUINOLINE ALKALOIDS (Cactus).

ANHYDRITE. A mineral consisting of calcium sulphate, $CaSO_4$, so named to distinguish it from the more common hydrated calcium sulphate, gypsum. From a pure aqueous solution calcium sulphate crystallises as gypsum, but when the solution is highly charged with salts (sodium, potassium and calcium chlorides and magnesium sulphate) it separates as anhydrite. Anhydrite crystallises in the orthorhombic system, but in its crystallographic characters it shows little analogy with the orthorhombic barium and strontium sulphates baryte and celestine, with which it would be expected to be isomorphous. An important character is the cleavage in three directions parallel to the axial planes of symmetry ; the mineral, therefore, breaks up into cubes like rock-salt. Well-formed crystals are not common ; they have been found in the salt-deposits of Germany and Austria, and in dolomite-rock in the Simplon tunnel, in Switzerland. Usually the mineral occurs as compact, granular masses of a white, grey, reddish or bluish colour, and resembling marble in appearance. Sp.gr. 2·9-3·0 ; hardness 3-3½, being considerably higher than gypsum. It is of frequent occurrence as layers interbedded in deposits of gypsum and rock-salt. The " anhydrite region " forming the base of the Prussian salt-deposits consists of alternating beds of anhydrite and rock-salt. Bands of anhydrite also occur throughout the salt-deposits, and are known to the miners as " year-rings." In contact with water anhydrite becomes altered into gypsum with an increase in volume of 60%. On this account galleries in the salt-mines when driven through beds of anhydrite gradually become closed up. Extensive beds of the mineral occur in the gypsum deposits of Nova Scotia and several other parts of Canada and in the United States. The salt dome at Winnfield in Louisiana is covered by a cap of anhydrite 105 ft. in thickness. In the red rocks of Permian and Triassic age of the North of England anhydrite is abundant in depth. For example, in the new shaft of the Hatfield Colliery, near Doncaster, a bed of anhydrite 19 ft. thick was penetrated at a depth of 201 yds. ; and thick beds have been met with in several deep borings in County Durham, and it is also recorded from Cumberland, Westmoreland, Yorkshire, Staffordshire, Leicestershire, Nottinghamshire, Derbyshire and Cheshire. For details of British occurrences, *see* " Special Reports on the Mineral Resources of Great Britain," vol. iii, Gypsum and Anhydrite, Mem. Geol. Survey, London, 1915 ; 2nd ed., 1918.

Until quite recently little use has been made of anhydrite, and it still accumulates in large quantities on the waste heaps of the gypsum quarries at several places in Canada. Trials have been made in the production of anhydrite plasters. It is now much used in the manufacture of ammonium sulphate for use as a fertiliser. Synthetic ammonia and carbon dioxide are passed through an aqueous suspension of the powdered mineral and the calcium carbonate formed as a by-product is used in the manufacture of Portland cement. For this purpose nearly half a million tons per annum are now mined at Billingham, Co. Durham.

A bluish-violet, compact variety known as " vulpinite," from Vulpino in Lombardy, has been used as an ornamental stone. Similar material of a delicate blue or bluish-grey colour from Cropwell Bishop in Nottinghamshire and other English localities takes a good polish and has been cut as small ornaments.

Reference.—L. H. Cole and R. A. Rogers, " Anhydrite in Canada," Canada Mines Branch, 1930, No. 719, p. 24 ; 1933, No. 732. L. J. S.

ANILINE.—**Historical.**—A substance called " Krystallin " was first obtained in 1826 by Unverdorben among the products of the destructive distillation of indigo. Eight years later Runge found a substance which he named " Kyanol " in coal tar. In 1840 Fritzsche obtained his " aniline " by distilling indigo [*Indigofera anil* (Linn.)] with alkali hydroxides. In the same year Zinin obtained what he called " benzidam " by reduction of nitrobenzene with hydrogen sulphide. It was left to Hofmann (1843) to show that all the above substances were identical and that nitrobenzene could be reduced to aniline by means of zinc and dilute acids. Perkin's discovery of *mauveine* in 1856 gave rise to a commercial demand for aniline and manufacture was commenced in this country the next year.

Preparation.—The methods employed for the preparation of aniline on the commercial scale depend on either the reduction of nitrobenzene or the reaction of chlorobenzene with ammonia. Nitrobenzene is obtained by nitration of benzene with a mixture of nitric and sulphuric acids, and several different methods of reduction are applicable.

(1) *Iron Reduction of Nitrobenzene.*—Reduction is effected by means of iron turnings and water in the presence of a small amount of a catalyst to start the reaction. The catalyst originally used was hydrochloric acid, but more recently ferrous chloride or alternatively mother liquors from the manufacture of aniline salt have been employed. The mechanism of the reduction process is complicated, and it is probable that the following three reactions all take place :

$$\text{(i)}\quad C_6H_5{\cdot}NO_2+2Fe+4H_2O \rightarrow C_6H_5{\cdot}NH_2+2Fe(OH)_3$$

$$\text{(ii)}\quad 2C_6H_5{\cdot}NH_2+FeCl_2+2H_2O \rightarrow 2C_6H_5{\cdot}NH_2,HCl+Fe(OH)_2$$

$$\text{(iii)}\quad 2C_6H_5{\cdot}NH_2,HCl+2Fe(OH)_2+2Fe \rightarrow 2C_6H_5{\cdot}NH_2+FeCl_2+Fe_3O_4+2H_2$$

The net result is expressed approximately by the equation :

$$9Fe+4H_2O+4C_6H_5{\cdot}NO_2 \rightarrow 4C_6H_5{\cdot}NH_2+3Fe_3O_4$$

A full discussion is given by Raikow (Z. angew. Chem. 1916, **29**, 196).

A typical plant used for the manufacture of aniline by the iron reduction method is illustrated diagrammatically in Fig. 1. The reducer consists of a cylindrical cast-iron vessel of capacity up to 1,600 gallons, fitted with cast-iron side and bottom lining plates which are renewable when they become worn through the wearing action of the iron borings. There is a run-off tap at the bottom for discharging the contents of the vessel, and there are also fitted charge holes for iron borings and nitrobenzene. The cast-iron agitator is driven by bevel gears and is frequently mounted on a hollow steel shaft, which serves as a steam inlet pipe. At other times a special steam pipe is let in through the roof or sides. A vapour pipe leads from the lid upwards to the condenser, from which a branched pipe leads the condensate either back to the reducer or to the separating tanks as required.

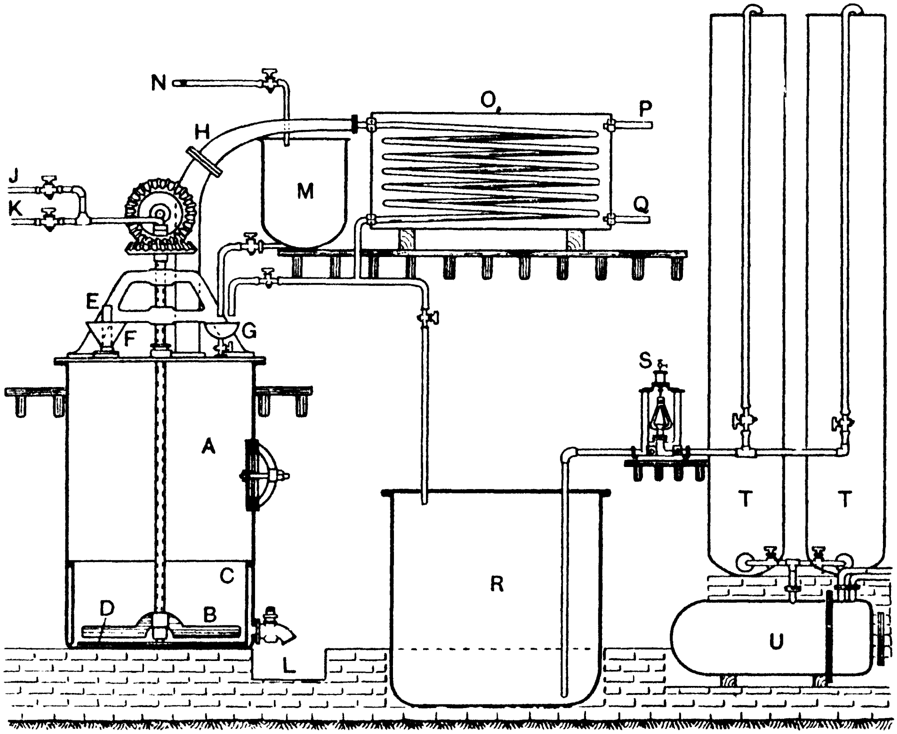


Fig. 1.—Aniline Oil Plant.

A, Reducer.
B, Agitating blades.
C, Side lining plates.
D, Bottom do.
E, Wood plug for hopper.
F, Charge hole for borings.
G, Charge hole for nitrobenzene.
H, Vapour pipe to condenser.
J, Steam inlet pipe.
K, Aniline steam do.
L, Gutter.
M, Receiving pan.
N, Pipe from N.B. tank.
O, Condenser.
P, Overflow.
Q, Cold water inlet.
R, Separating tank.
S, Steam pump.
T, Settling tubes.
U, Air pressure egg.

The plant may be operated on the following lines. A portion of the total charge of iron borings together with aniline water (from the separating tanks) and the catalyst (hydrochloric acid, ferrous chloride, or aniline salt mother liquors) are charged into the reducer and steam turned on until refluxing commences. A proportion of the nitrobenzene charge is now run in slowly at such a rate that the heat of reaction serves to keep the mixture boiling without introducing further steam. Thereafter further alternate additions of iron and nitrobenzene are made at a rate suitable for controlling the reflux. If the temperature of reduction is too low, azoxy compounds are formed which are difficult to reduce, and if the reaction is allowed to become too vigorous, there is a loss of yield due to the formation of benzene. An alternative method is to start by charging in all the nitrobenzene and to regulate the reaction by gradual charging of the iron and catalyst. Refluxing is continued until reduction is complete, *i.e.* the refluxing oil is completely soluble in dilute acid.

The next stage of the process is the separation of the crude aniline from the aqueous liquor and sludge in the reducer. The best known procedure is by blowing in steam, whereby the aniline is distilled off, passing through the condenser to separating tanks. In these tanks the aniline and water are allowed to separate, the oil being passed on for rectification and the water which contains aniline in solution (approx. 2–3%) used for generating steam for use in the process. Two alternative methods may be mentioned. In the one, the aniline is siphoned off after the whole has been allowed to settle; in the other, the water and aniline are distilled directly from the sludge in an agitated, gas-fired, "heavy duty" still.

The crude aniline oil is finally purified by rectification, *i.e.* distillation under vacuum. The still (*see* Fig. 2) consists of a large horizontal wrought-iron cylindrical tank, approx. 8 ft. in diameter by 15 ft. long. Heating is effected by passing high-pressure steam through internal wrought-iron pipes of 2 in. diameter, which lie horizontally in the still. The vapours from the still pass up a column 8 in. in diameter and 12 ft. high, and thence to a coil surrounded by water, where they are condensed. From the condenser a branched pipe leads to two receivers, and when one is full (as indicated by a sight glass) it is disconnected and the oil allowed to flow to the second receiver. The distillation may thus be carried on without interruption.

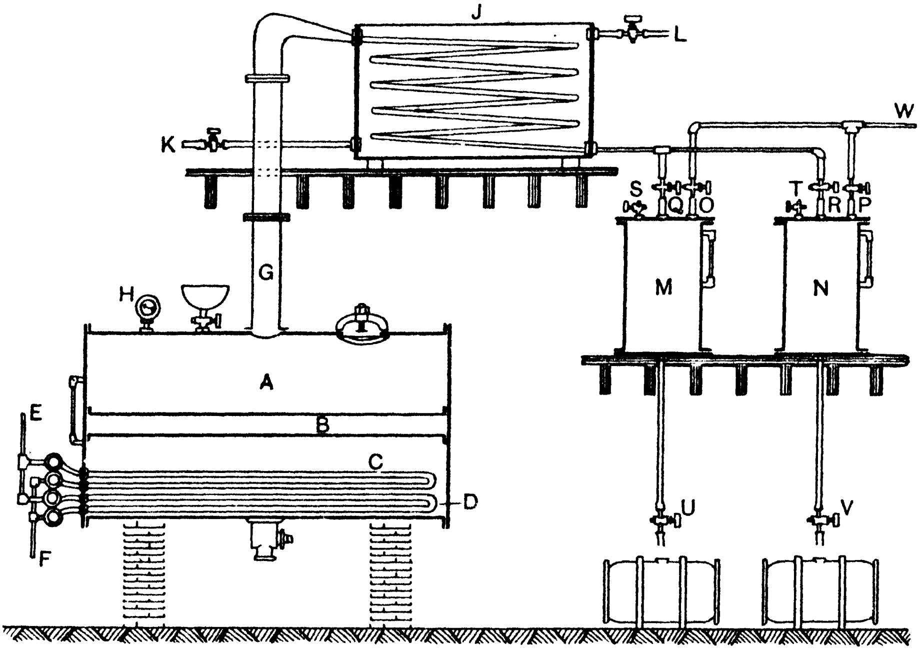


Fig. 2.—Vacuum Still for Aniline Oil.

A, Vacuum still.
B, Internal hollow stay.
C, Steam tubes.
D, Do. do.
E, Steam inlet.
F, Do. outlet.
G, Vapour pipe to condenser.
H, Pressure gauge.
J, Condenser.
K, Cold-water inlet.
L, Overflow for water.
M, Receiver for distilled oil.
N, Do. do. do.
O, Connection from vacuum pump.
P, Do. do. do.
Q, Inlet from condenser.
R, Inlet from condenser.
S, Air-admission tap.
T, Do. do.
U, Run-off tap for distilled oil.
V, Do. do. do.
W, Connection from vacuum pump.

The still is charged with crude aniline and a vacuum of 29 in. applied. Steam is then passed through the coils until distillation begins. The first runnings (approx. 7%) contain much water and these are returned to the "crude" settling tanks, and after this the temperature rises rapidly to about 90°–95°C., when the distillate contains but little water. When no more water can be perceived (approx. 4% more of distillate), the flow of distillate is directed to the receiver for refined oil. The small residue (approx. 3%) remaining in the still after distillation is returned to the reducers and worked up again.

The iron oxide sludge obtained in the reduction operation is allowed to settle as much as possible from the water and when dried and ground finds a use in the purification of coal gas from sulphur.

Large quantities of sludge are also used for the manufacture of cheap black paints. Recent patent literature reveals attempts, mainly in Germany, so to modify the conditions of reduction that the resulting oxide sludge is obtained in a form more valuable for the production of pigments. Thus B.P. 279283 states that when the concentration of catalyst exceeds 6% the black oxide is in a particularly fine state of division. According to B.P. 263376, reduction in the presence of aluminium chloride gives a red or violet-red oxide. In B.P. 314573 the aluminium chloride is replaced by salts of other bi- and tri-valent metals such as Ce, La, or Dy. In B.P. 394027 reduction is carried out in the presence of lead compounds, the shade of the resulting pigment depending on the amount of lead used. In B.P. 374793 reduction is effected in the presence of phosphoric acid, and the sludge is calcined to give red to violet pigments.

(2) *Catalytic Reduction of Nitrobenzene.*—Catalytic reduction of nitrobenzene to aniline is effected by passing the vapours of nitrobenzene together with hydrogen or water-gas over a catalyst heated to a suitable temperature (120°–300°C.). If too high a temperature is used, an over-reduction occurs, resulting in the formation of benzene and ammonia and hydrogenation of the benzene ring. In order to control the temperature the nitro-compound is therefore volatilised with steam and the catalyst is heated to the same temperature as the mixture of steam and nitro-compound. A tank of nitrobenzene is heated to 120°C. and a mixture of superheated steam and hydrogen passed in. The vapours are led at such a rate through horizontal tubes containing catalyst heated externally to 120°C. that complete reduction occurs. The resulting mixture of aniline and water is then separated and rectified as in the iron reduction process, the aniline-water being used to generate the steam required for the operation.

The patent literature describes the use of many different catalysts. Thus copper is claimed in B.P. 13149, 15334 (1914); 5692, 6409 (1915); U.S.P. 1207802; G.P. 139457; nickel in B.P. 16936, 22523 (1913), G.P. 282492, and F.P. 458033; iron and its oxides in F.P. 462006 and G.P. 281100; silver and gold in G.P. 263396. In B.P. 297212 sulphur is added to the catalyst in order to slow down the reaction and prevent formation of by-products. U.S.P. 1639186 describes a catalyst composed of silica gel upon which is deposited reducible oxides of heavy metals such as **Fe**, **Ni**, or **Cu**. In G.P. 441433 oxides of **Zn**, **Cu**, **V**, **Cd**, **Mn**, **W** are claimed as catalysts. G.P. Appn. I. 27961 describes the preparation of **Ni**, **Co**, or **Cu** catalysts by displacement from solutions of their salts by more electro-positive elements. According to Irlin (B. 1933, 581) a catalyst consisting of **Cu**, containing 10% of lime, at 240°–250°C. effects conversion of nitrobenzene to aniline in 96·5% yield. Adkins and Connor (J. Amer. Chem. Soc. 1931, **53**, 1091) describe the use of a copper chromite catalyst for nitro-compounds generally, including nitrobenzene. *See also* Legg and Adam (B.P. 166283); Brown and Heneke (J. Physical Chem. 1922, **26**, 161).

(3) *Other Methods of Reduction of Nitrobenzene.*—Sodium disulphide solution forms a very good reducing agent for nitro-compounds (G.P. 144809). The requisite amount of sulphur is dissolved in a hot concentrated solution of sodium sulphide and the nitro-compound charged in gradually at such a rate that the heat of reaction serves to maintain the reduction. The reaction proceeds according to the equation:

$$RNO_2 + Na_2S_2 + H_2O \rightarrow RNH_2 + Na_2S_2O_3$$

This method is more useful for the reduction of certain substituted nitrobenzenes than for nitrobenzene itself.

Electrolytic reduction is described in the patent literature, but this does not appear to compare favourably with other methods.

(4) *Amination of Chlorobenzene.*—The preparation of aniline by the action of ammonia on chlorobenzene in the presence of copper sulphate has been known for many years (B.P. 3966, 1908), and the method is now used extensively in America. Copper compounds are used as catalysts, and it has been shown by Quick (J. Amer. Chem. Soc. 1920, **42**, 1033) that cuprous compounds are the active agents. U.S.P. 1607824, 1726170, 1726173 contain descriptions of the process, which is briefly as follows:

Chlorobenzene together with 4–5 molecular proportions of ammonia (25%) and 0·1–0·2 molecular proportions of Cu_2O or Cu_2Cl_2 is heated in an iron autoclave for 6–12 hours at 150°–250°C. A pressure between 500 and 1,500 lb./in.^{2} develops. At the completion of the reaction, the contents of the autoclave are blown into a closed container and treated with sufficient caustic soda to decompose the ammonium chloride and neutralise the small amount of phenol which is formed as a by-product. Steam is now blown in and there are distilled off, in order, ammonia, unchanged chlorobenzene, aniline and diphenylamine. A precipitate of copper compounds remains and as this possesses catalytic activity it is washed and used in the next charge. According to Woroshzow and Kobelew (Chem. Zentr. 1935, **106**, II, 505) the yield of aniline is 90% of the theoretical, phenol 4–5%, and diphenylamine 1–2% being also formed.

In place of a cuprous compound it is possible to use a cupric compound together with sufficient copper to bring about reduction *in situ* to the cuprous state. In U.S.P. 1885625 a reducing agent such as glucose is used to keep the copper in the lower state of oxidation.

The ammonium chloride which is formed as a product of reaction has a retarding influence, and in order to counteract this cuprous oxide is added to destroy it as it is formed. Furthermore, ammonium chloride introduces corrosion problems and B.P. 370774 recommends the presence of an alkaline earth oxide to bring about decomposition.

(5) *Amination of Phenol.*—According to Fischer, Bahr, and Wiedeking (Brennstoff-Chem. 1934, **15**, 101), when phenol and ammonia are passed over alumina at 10 atmospheres pressure and at a temperature of 450°–480°C., there is over 90% conversion to aniline. Oxides of **Th**, **Ti**, **W**, **Mo**, and **V** are also mentioned as catalysts (*see also* Chem. Ztg. 1934, **32**, 620).

Valuation of Commercial Aniline Oil.—Owing to the extent of the experimental error, chemical methods of evaluating the purity of commercial aniline oil are inaccurate when the purity exceeds 99·5%. In consequence, physical methods are employed. Specific gravity, freezing-point and boiling range are the properties commonly examined and the two latter furnish an excellent assessment of the purity of the sample. The specific gravity of pure aniline is given as 1·0268 at 15°C.

The method used for determination of the boiling range is as follows. An amount of 100 ml. is introduced into a standard size distillation flask and distilled at a standard rate through a short condenser into a measuring cylinder. The thermometer reading is noted when the first drop distils and again when 95 ml.

have distilled over. Pure aniline has a boiling-point of 184·4°C./760 mm. and if the temperature rises considerably above this figure towards the end of the distillation, the presence of toluidine as an impurity may be suspected. The presence of sulphur in the aniline is indicated by the evolution of hydrogen sulphide during the distillation.

The freezing-point, which is probably the best criterion of purity, is determined as follows. The sample of aniline is dried to practically constant moisture content (0·01–0·15%). 100 ml. are transferred to a 250-ml. glass-stoppered bottle and shaken well with 0·2 ml. of water. Powdered potassium hydroxide (10 g.) is now added and the whole is kept for 2 hours with occasional shaking.

About 40 ml. of the clean aniline is decanted into a crystallising tube consisting of a boiling tube 6 in. by 1 in. surrounded by a slightly wider tube which serves as an air jacket. The crystallising tube is fitted with a cork bearing the thermometer and a glass stirrer (for diagram *see* "Standard Methods for Testing Tar and its Products," p. 80). The whole is immersed in a freezing bath, temperature of which should not be lower than −16°C. The aniline is stirred continuously but gently, taking temperature readings every half-minute. The oil first becomes supercooled, and when crystallisation occurs the temperature rises again. The readings are continued at half-minute intervals for five minutes after the temperature rise has started, and the crystallising point corresponds with the first five consecutive readings during which the temperature remains constant within 0·05°C. If the temperature does not remain constant for five readings, the readings before the rise and those after the rise are plotted against time. The point of intersection of the curves is the crystallising point. A good sample of technical aniline oil should have a crystallising point of −6·4°C., which is practically the figure recorded for the pure material.

In order to detect the presence of either nitrobenzene or insoluble hydrocarbons, 10 ml. of the sample are dissolved in 90 ml. of dilute hydrochloric acid. If these impurities are absent, the solution is quite clear. If any oily drops are present or if the solution is opaque, then it is steam-distilled. If nitrobenzene is present, this passes over into the distillate and may be reduced to aniline, which is determined quantitatively by titration with $N/10$ potassium bromate solution, and the amount of nitrobenzene in the original aniline thus assessed.

Impure samples of aniline darken considerably on storage and according to Bulitsch (B. 1934, 85) this may be due to the presence of thiophen in the original benzene, to the contamination of the iron turnings used in the reducer with unsaturated oils or to the presence of diamines due to over-nitration of benzene. The darkening is accelerated by air and light and may be minimised either by the addition of 0·05% of oxalic acid or by storing in an inert atmosphere.

Salts and Double Compounds of Aniline.—Aniline forms crystalline salts with mineral and organic acids, *e.g.* sulphuric, hydrochloric, acetic, and oxalic. The hydrochloride, $C_6H_5{\cdot}NH_2{\cdot}HCl$, is the best known of these and is manufactured in large quantities as *aniline salt.* It is used by calico printers for the production of aniline black, for which purpose it is required in a pure condition, free from sand or grit of any kind.

The manufacturing process consists of mixing the calculated amounts of aniline with pure concentrated hydrochloric acid (approx. 36% strength) in lead-lined or earthenware tanks. The mass is allowed to cool and the crystals are separated from mother liquors by centrifuging, the basket being either lead-lined or made of ebonite. The mother liquors are used in place of hydrochloric acid in the reduction of nitrobenzene, or the aniline may be recovered by basification and steam distillation. Pure aniline hydrochloride forms large white crystals having a melting-point of 198°C.

Aniline hydrochloride forms double salts with several metallic chlorides; with platinic chloride, for example, there is formed a yellow crystalline compound, $(C_6H_5{\cdot}NH_2{\cdot}HCl)_2PtCl_4$, of melting-point 245°C. It also forms double salts with cuprous and cupric chlorides. With 1 : 3 : 5-trinitrobenzene aniline forms a double compound, m.p. 123°–124°C. W. A. S.

ANILINE BLACK. An insoluble black pigment which is produced by the oxidation of aniline in acid solution. For producing aniline black on the fibre, *see* DYEING. For constitution, *see* Green and Woodhead (J.C.S. 1910, **97**, 2388; 1912, **101**, 1117).

ANILINE-BLUE, -BROWN, -RED, -SCARLET. Triphenylmethane dyestuffs.

ANILINE ORANGE, a nitro-dyestuff, is a mixture of the ammonium or potassium salts of dinitro-*o*-cresol and dinitro-*p*-cresol.

ANILINE VIOLET. Syn. for Mauveine or Perkin's Violet (*see* AZINE DYESTUFFS).

ANILINE YELLOW, a nitro-dyestuff, is the alkali salt (Na, NH_4 or less commonly Ca) of 2 : 4 dinitro-α-naphthol.

ANIME or **ANIMI** is elemi, *q.v.*

ANISALDEHYDE, $MeO{\cdot}C_6H_4{\cdot}CHO$, sp.gr. 1·127, *n* 1·573, b.p. 91°/4 mm., 248°/760 mm., has a pronounced hawthorn odour, and is used in synthetic perfumery under the name *aubepine.* It blends well with acetophenone and is much esteemed in such artificial perfumes as wallflower, acacia, sweet pea, cloves, orchid, etc. E. J. P.

ANISEED (*Anis*, Fr., Ger.). The fruit of the *Pimpinella Anisum* (Linn.), N.O. *Umbelliferæ* is indigenous to Asia Minor and Egypt, and is also cultivated in Russia, Malta, Spain, Germany and other parts of Europe. It is used for the preparation of true aniseed oil and alcoholic liqueurs, one liqueur which has aniseed as its principal flavouring being named after it. Its alcoholic extracts vary from 7·6 to 36·24% and it has an ethereal oil content of 0·4 to 2·8% (Biechele, Pharm. J. [3], **10**, 878, and Benedek, Kiserletiigyi Közleminyék, 1933, **36**, 216–20). True aniseed oil contains anethole 80–85%, methyl chavicol, anisyl acetone and traces of acetaldehyde. F. G. H. T.

ANISE OIL (*see* OILS, ESSENTIAL). There are two sources of this oil, both of which yield an oil practically identical in character and composition. The oil distilled from the fruit of *Pimpinella Anisum* (Linn.), N.O. Umbelliferæ, grown in Europe, is used for liqueurs. The chief source of anise oil of commerce is the Star Anise, *Illicium verum* (Hook), N.O. Magnoliaceæ. This oil is imported from China. The yield of oil from the star anise fruits is 2 to 4%, whilst the pimpinella anise seldom yields more than 2%.

The characters of star-anise oil are: sp.gr. 0·975–0·990 at 20°/15°, opt. rot. 0° to −2°, occasionally slightly dextrorotatory; n_D^{20} 1·552–1·558; soluble in 3 vols. 90% alcohol. It congeals about 15°, remelting at 17° to 19°.

Star-anise oil contains anethole,

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_3}\ (1:4),$$

80–90%, methyl chavicol,

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH:CH_2},$$

anisaldehyde, anisic acid, anisyl acetone,

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CH_3},$$

pinene, phellandrene, limonene, cineole and safrole. Important changes take place in the oil on keeping, the melting-point being lowered and the density increasing. It is employed medicinally as a carminative and expectorant and as a flavouring agent. C. T. B.

ANISIC ACID, *p*-methoxybenzoic acid, $\mathrm{MeO{\cdot}C_6H_4{\cdot}COOH}$, colourless needles or prisms, m.p. 135°, b.p. 280°, is obtained by the oxidation of anethole (*p*-methoxy-allylbenzene), and can be prepared by methylating *p*-hydroxybenzoic acid, or from *p*-bromoanisole by the Grignard reaction.

ANISIDINE, $\mathrm{NH_2{\cdot}C_6H_4{\cdot}OCH_3}$. o-*Anisidine* is obtained by reducing *o*-nitroanisole with tin or iron and hydrochloric acid (G.P. 7217, 1878; Vermeulen, Rec. trav. chim. 1906, **25**, 20), by heating *o*-methoxybenzamide with a hypochlorite and caustic alkali (Tcherniac, B.P. 282907), or by heating under pressure a mixture of *o*-aminophenol, potassium methyl sulphate and potassium hydroxide solution. It is a colourless liquid, m.p. 5·2° (Schneider, Z. physikal. Chem. 1897, **22**, 234), b.p. 225° (Perkin, J.C.S. 1896, **69**, 1210), and d^{26} 1·108. The density at other temperatures has been determined by Perkin (*ibid.* 1211). It is used for the production of AZO-DYESTUFFS (*q.v.*). Acetylation by acetic anhydride (Mühlhäuser, Annalen, 1881, **207**, 242; Körner and Wender, Gazzetta, 1887, **17**, 492; Kaufmann, Ber. 1909, **42**, 3482) or glacial acetic acid (Herold, Ber. 1882, **15**, 1685) yields the *acetyl derivative*, m.p. 87°–88° (Kaufmann), and b.p. 303°–305° (Mühlhäuser). The *formyl derivative*, m.p. 129°–129·5°, is obtained by boiling with formic acid (Bamberger, Ber. 1903, **36**, 2052), and the *benzoyl derivative*, m.p. 59·8°, by the action of benzoyl chloride (Mühlhäuser, Annalen, 1881, **207**, 244). Four molecules of *o*-anisidine react with one of hydroferricyanic acid to give a hydroferricyanide (Cumming, J.C.S. 1924, **125**, 2541).

m-*Anisidine* is obtained by reducing *m*-nitroanisole with tin or zinc and hydrochloric acid, or with alcoholic sodium sulphide. It is an oily liquid, b.p. 251° (Pfaff, Ber. 1883, **16**, 614 and 1139) or 243·5°/755·5 mm. (Körner and Wender, Gazzetta, 1887, **17**, 492). The *acetyl* derivative has m.p. 80°–81° (Körner and Wender).

p-*Anisidine* is obtained by reducing *p*-nitroanisole with tin and hydrochloric acid or with alcoholic ammonium or sodium sulphide or electrolytically (Kirkhgof, Khim. Farm. Prom. 1933, 326; B. 1934, 872). It crystallises in prisms, m.p. 57·2° and b.p. 243° (Perkin, J.C.S. 1896, **69**, 1211). *p*-Anisidine and its substitution derivatives are used for the production of azo-colours, and its condensation compound with orthoformic ester has anæsthetic properties (Goldschmidt, B.P. 9792; J.S.C.I. 1899, **18**, 606). The *acetyl derivative*, m.p. 127° (Körner and Wender, Gazzetta, 1887, **17**, 493; Pawlewski, Ber. 1902, **35**, 111; Reverdin and Bucky, Ber. 1906, **39**, 2689), is an antipyretic and antineuralgic, its physiological action has been investigated by Hinsberg and Treupel (Arch. exp. Path. Pharm. 1893, **33**, 231). The *formyl derivative*, m.p. 80°–81°, is obtained by boiling with formic acid (Fröhlich and Wedekind, Ber. 1907, **40**, 1009) or ethyl formate (Bayer and Co., G.P. 49075). The *benzoyl derivative*, m.p. 156°, is obtained by the action of benzoyl chloride (Reverdin, Ber. 1909, **42**, 1524).

ANISOLE. Methyl phenyl ether,

$$\mathrm{C_6H_5{\cdot}O{\cdot}CH_3}$$

Anisole may be obtained by distilling *o*-methoxybenzoic acid (anisic acid) with barium hydroxide, by heating potassium phenate with methyl iodide at 120° (Cahours, Ann. Chim. Phys. 1842 [iii], 2, 274; 1844, **10**, 353; 1849, **27**, 439), by passing methyl chloride over dry sodium phenate at 190°–200° (Vincent, Bull. Soc. chim. 1883 [ii], **40**, 106), by heating phenol with methyl alcohol and potassium bisulphate (G.P. 23775), by fusing sodium benzenesulphonate with sodium methoxide (Moureu, J. Pharm. Chim. 1883 [v], **8**, 211). It is prepared in 72–75% yield by treatment of sodium phenate with dimethyl sulphate (Hiers and Hager, Organic Syntheses, 1929, **9**, 12).

Properties.—Anisole is a colourless liquid, b.p. 155°, m.p. −37·8°, and d^{18} 0·991.

Derivatives.—By the action of phosphorus pentachloride, the p-*chloro*-compound is formed, containing some 10% of the *o* derivative (Hayashi, J. pr. Chem. 1929, **123**, 289). Blicke and Smith (J. Amer. Chem. Soc. 1928, **50**, 1229) describe a modification of the method of Brenans (Bull. Soc. chim. 1901 [iii], **25**, 819) whereby the yield of p-*iodoanisole* from anisole with mercuric oxide and iodine in alcohol is increased to 73%. The same product is obtained from *p*-anisidine by the diazo-reaction in 75–80% yield, but direct reaction of iodine monochloride with anisole gives a mixed product. Bures and Soucek have described a method of preparing the halogen derivatives using the 3:4-dibromoanisidine (Chem. Zentr. 1929, I, 1098). The nitration of anisole has been studied by Griffiths, Wakely, and Watson (J.C.S. 1934, 631), who obtained a 70% yield of the *ortho*-compound using acetyl or benzoyl nitrate.

Addition compounds between anisole and various mercuric salts have been described by Manchot (Annalen, 1920, **421**, 316) and Dimroth (Ber. 1921, **54** [B], 1504).

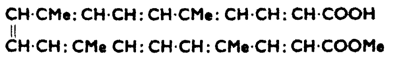
ANKERITE. A member of the group of rhombohedral carbonates containing calcium, magnesium and iron, with sometimes a little manganese. The formula is like that of dolomite with the magnesium partly replaced by iron, for normal ankerite it is $CaCO_3 \cdot Mg,Fe\ CO_3$. The angle between adjacent faces of the rhombohedral cleavage is 73° 48′. D 2·95–3·1 ; H 3½–4. The mineral forms white, greyish or brownish cleavage rhombs, cleavage masses or granular masses. It occurs in some abundance with chalybite ($FeCO_3$) in the iron mines of Eisenerz in Styria, Londonderry in Nova Scotia and in northern New York. The white, thin platy seams often seen in coal consist usually of ankerite (T. Crook, Min. Mag. 1912, **16**, 219 ; L. Hawkes and J. A. Smythe, *ibid.* 1935, **24**, 65).

L. J. S.

ANNATTO (*Arnatta*, *Rocou*). The colouring matter from the seeds of *Bixa orrellana* (Linn.), a small shrub found in Central and Southern America. Three kinds are marketed, Spanish annatto from Brazil, flag or French annatto from Cayenne, and Dutch annatto from the New Orleans district. Whilst the popularity of annatto for dyeing in the textile industry has waned due to its sensitivity to light, it is still used on the Continent for colouring foodstuffs such as butter and cheese and is employed in the manufacture of varnishes. Its dyeing properties must have reached civilisation through the South American Indians, who used annatto as a war paint. The principal pigment is *bixin*, a member of the carotenoid series (*see* CAROTENOIDS).

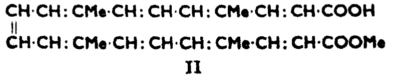
Bixin, $C_{25}H_{30}O_4$, best extracted by the method of Kuhn and Ehmann (Helv. Chim. Acta, 1929, **12**, 904), crystallises from glacial acetic acid in glistening violet-red needles. m.p. 198°, which are stable in the crystalline state but undergo autoxidation in solution. Herzig and Faltis (Annalen, 1923, **431**, 40) showed that the natural pigment is the monomethyl ester of a dicarboxylic acid, *norbixin*, and that methylation of either bixin or norbixin gives the dimethyl ester, *methylbixin*. They also demonstrated that 9 molecules of hydrogen are required to saturate bixin, giving the oily *perhydrobixin* which yields *perhydronorbixin* on hydrolysis.

Kuhn and Winterstein (Helv. Chim. Acta, 1928, **11**, 427) observed that bixin on controlled oxidation gave methylglyoxal and methyl β-acetylacrylate, and that complete oxidation furnished 4 molecules of acetic acid. They therefore proposed the unsymmetrical formula (I), as this apparently explained the existence of an isomeric series which had been observed in practice (*see* later). These authors (Ber. 1932, **65** [B], 646) later changed this formula to a symmetrical one (II), thus bringing it into alignment with lycopene, which had been shown by Karrer (*see* LYCOPENE) to possess such symmetry. Confirmation of this constitution was provided by the synthesis of perhydronorbixin by Karrer *et al.* (Helv. Chim. Acta, 1932, **15**, 1218, 1399) and also by the degradation by means of regulated oxidation of lycopene through bixin dialdehyde to bixin (Kuhn and Grundmann, Ber. 1932, **65** [B], 1880).



$$\begin{array}{l} CH\cdot CMe:CH\cdot CH:CH\cdot CMe:CH\cdot CH:CH\cdot COOH \\ \| \\ CH\cdot CH:CMe\ CH:CH\cdot CH:CMe\cdot CH:CH\cdot COOMe \end{array}$$

I



$$\begin{array}{l} CH\cdot CH:CMe\cdot CH:CH\cdot CH:CMe\cdot CH:CH\cdot COOH \\ \| \\ CH\cdot CH:CMe\cdot CH:CH\cdot CH:CMe\cdot CH:CH\cdot COOMe \end{array}$$

II

Several modifications of bixin and its derivatives are known and for a long time the lack of any complete knowledge of their relationship to one another hindered the complete elucidation of the structure of the pigment. The investigations of Karrer, Helfenstein, Widmer, and van Itallie (Helv. Chim. Acta, 1929, **12**, 741), Kuhn and Winterstein (Ber. 1932, **65** [B], 646), and Kuhn and Drumm (*ibid.* 1458) have now completely clarified the position, the relationship being one of geometrical isomerism. The members of the series are :

Bixin (labile bixin, ordinary bixin, or bixin II) (for properties, *see* earlier).

Stable bixin (β-bixin, *iso*bixin, or bixin I) crystallises from glacial acetic acid in yellow rhomboids, m.p. 215°–220°, and is less soluble than ordinary bixin. The greater solubility of the labile members is observed throughout the series.

Norbixin (labile norbixin) crystallises from glacial acetic acid in needles, m.p. 250°–255° and is readily soluble in dilute alkalis.

Stable norbixin (*iso*norbixin, β-norbixin) separates from glacial acetic acid in leaflets, m.p. above 300°, and is difficultly soluble in alkalis.

Methylbixin (labile methylbixin) crystallises from a mixture of chloroform and ethyl alcohol in plates, m.p. 163°–164°.

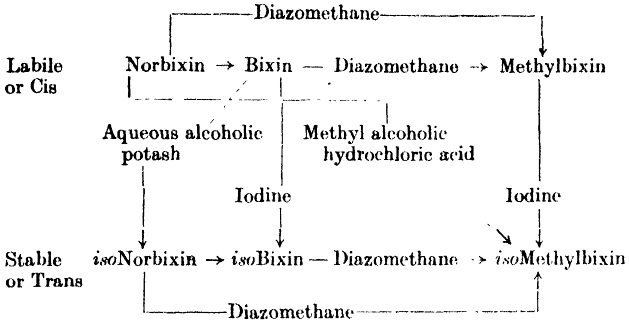
Stable methylbixin (*iso*methylbixin, β-methylbixin) crystallises from ethyl acetate in violet needles, m.p. 205°–206°.

The absorption spectra of the various members of the series, and their relationship are shown in Tables I and II respectively.

TABLE I.

Substance.	In carbon disulphide.	In chloroform.
	mμ	mμ
Labile norbixin .	527,491,458	503,469,440
,, bixin . .	523,489,457	503,469,439
,, methylbixin	520,485,454	503,469,441
Stable norbixin .	527,492,457	509,475,442
,, bixin . .	526,491,457	509,475,443
,, methylbixin	525,490,456	509,475,444

TABLE II.


Diazomethane
Labile or Cis
Norbixin → Bixin — Diazomethane → Methylbixin
Aqueous alcoholic potash
Methyl alcoholic hydrochloric acid
Iodine
Iodine
Stable or Trans
*iso*Norbixin → *iso*Bixin — Diazomethane → *iso*Methylbixin
Diazomethane

I. M. H. and R. F. P.

ANNEALING (*le recuit*, Fr. ; *die Glühbehandlung*, Ger.). A process applied to glass, metals and alloys, usually for the purpose of rendering them softer and less brittle or of removing internal stresses. The annealing treatment involves the application of heat generally followed by slow cooling and may effect its object mainly by :

1. The removal of internal stresses from cast, wrought, or welded material.
2. The removal of effects of deformation or "cold work."
3. The production in alloys, subject to a phase change on cooling, of a structure approaching equilibrium conditions (*see* METALLOGRAPHY).

Two or all of these effects may result from one annealing operation.

Annealing to remove internal stresses is necessary with many types of casting. When a metal casting is cooling in a mould from solidification to room temperature there is in general a lack of uniformity in temperature, particularly in large castings or castings of unequal section, which results in a non-uniform contraction. The outer or most rapidly cooled layers become hard and rigid while other portions are still at a higher temperature. Contraction of these parts is consequently restricted by the rigidity of the cooler portions and stresses are set up in the casting which may in some cases reach a high order. These stresses are relieved by slight plastic flow if the casting is heated uniformly to a sufficiently high temperature, but cooling must then be sufficiently slow to maintain a uniform temperature throughout if further internal stresses are not to be set up. The origins of internal stresses in wrought or welded material may be different from those in castings, but the principles involved in the removal of such stresses by annealing are the same.

Internal stresses are more likely to be present to a dangerous extent in poor conductors such as glass. The outer layers of glass become rigid long before the interior, resulting in contraction stresses which may be sufficiently high to cause sudden fracture. Reheating the glass to a temperature at which it is soft enough to flow under these stresses must, however, with a material of such low thermal conductivity be followed by extremely slow cooling if an approximation to uniformity of temperature throughout the mass is to be attained. For a fuller discussion of the annealing of glass, *see* GLASS.

Probably the most important aspect of annealing as applied to metals is the removal of the effects of cold work. Cast metals consist of aggregates of small crystals. When the metal is deformed in the cold as by hammering, rolling, etc., these individual crystals are deformed in the same general sense as the mass of which they form a part and this deformation is accompanied by a hardening of the metal which imposes a limit on the amount of deformation possible without rupture. This hardening is partly due to an internal rearrangement in each crystal and partly, according to some authorities, to some local destruction of the crystalline arrangement resulting in the formation of a hard "amorphous" phase.

Beilby (Proc. Roy. Soc. 1903–4, A, **72**, 218) suggested that the surface film of a polished metal was amorphous in the sense that the flow occurring during polishing had destroyed the crystalline arrangement of the extreme surface layer, and this has subsequently been confirmed by Finch and his collaborators by the use of the method of electron diffraction (Proc. Roy. Soc. 1934, A, **145**, 676).

When cold-worked metal is subsequently annealed, *i.e.* heated to a suitable temperature, the metal recrystallises and becomes softer and more ductile, after which further cold work is possible. For instance, in the cold rolling of a 70/30 brass ingot to strip, the metal is annealed at about 600°–650°C. after each 50% reduction in thickness. The temperature at which recrystallisation occurs varies with different metals ; in some cases the metal recrystallises at ordinary temperatures, *e.g.* lead (Ewing and Rosenhain, Phil. Trans. 1900–01, A, **195**, 279). At low annealing temperatures the rate of recrystallisation is slow and a much longer time is needed for complete recovery than at higher temperatures. On the other hand, with nearly all metals the greater the amount of cold-work initially applied the lower the temperature at which the metal will recrystallise. The use of excessively high annealing temperatures, or "over-heating," causes an undue coarsening of the grain (*i.e.* a growth of crystal size) which is undesirable in many metals and alloys because of the consequent deterioration in mechanical properties. With the great majority of pure metals and with many alloys the rate of cooling after annealing is generally immaterial so far as the softening effect is concerned.

In certain metals and a large number of alloys, however, some change in constitution or structure occurs between the melting-point and room temperature, due, for instance, to an allotropic transformation or a variation of solid solubility of one constituent in another. In these cases the structure and properties of the alloy will be affected by the rate of cooling through the temperature range in which such changes occur. The most striking example is found in carbon steels ; a steel containing, for instance, 0·5% carbon is moderately soft if cooled slowly to a temperature below about 650°C., but becomes extremely hard if cooled suddenly (*i.e.* in water) from a temperature above about 700°C. In such cases annealing consists in raising the steel to a temperature above the transformation range and cooling sufficiently slowly to allow the structural changes to take place which are suppressed when the steel is hardened by quenching. In steels, the addition of special elements may affect considerably the temperatures at which these changes take place, and the rate at which the changes proceed. The response of the steel to heat treatment and the annealing treatment necessary to soften the steel are consequently altered materially. The addition of tungsten, for instance, in considerable percentages (*e.g.* 14 to 18% as in high-speed steels) has the effect of raising the annealing or softening temperature considerably, and tools made of such steels retain a cutting edge at a dull red heat (below 700°C.), at which temperature a carbon steel is useless. The softening of stainless steels of the 18% chromium–8% nickel type is a typical special case, in that the heat treatment applied between cold-working operations can hardly be termed a true annealing although frequently referred to as such. The steel is heated to a fairly high temperature (1,000°–1,200°C., depending on the carbon content), at which temperature the carbon is all taken into solution. Rapid cooling from this temperature preserves this solution and gives a comparatively soft material which can be worked further. Air cooling is sufficiently rapid for thin sheet metal, but slow cooling causes precipitation of carbide.

In non-ferrous metals and alloys heat treatment to give variations in properties is becoming increasingly important. Certain aluminium alloys are particularly susceptible to such treatments, which usually depend on an increased solubility of a second constituent as the temperature is raised. *Duralumin* is a well-known example, the best mechanical properties being obtained by quenching in water from about 480°C., giving a soft material which hardens on standing at room temperature. Duralumin is annealed by heating to between 350° and 400°C and slowly cooling, after which treatment no "ageing" occurs.

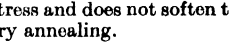
Variations of annealing treatment are frequently used for special purposes such as the "normalising" of steel to produce grain refinement, in which the steel is heated to a temperature above the upper limit of the critical range and allowed to cool freely in the air. A normalised steel is cooled more rapidly than an annealed steel and is therefore in general not fully annealed. "Low-temperature annealing," as applied to the relief of internal stresses in cold-worked non-ferrous metals, is another term deserving special definition. Cold-working not only hardens a metal by distorting the individual crystals but is capable of introducing internal stresses which may rise locally to very high values. A hollow sunk brass tube, for instance, is generally in a condition of severe internal stress, which can be relieved by heating the tube for a short time at a temperature from 250°–300°C. Such a low-temperature annealing permits only the relief of internal stress and does not soften the material as in ordinary annealing.

A point of increasing importance in metallurgical practice is the effect of the atmosphere in which the metal is heated during the annealing treatment. Heating in air causes more or less serious oxidation of most metals and alloys and necessitates some form of cleaning the surface before the material can be worked further. It is becoming increasingly common therefore to anneal in neutral or reducing atmospheres in order to preserve the surface free from tarnish or other form of chemical attack. Such a treatment is known as "bright annealing," the particular gas atmosphere employed in individual cases depending on the nature of the material under treatment. G. L. B.

ANODYNINE. Antipyrine, *q.v.*

ANOGON. *Meriodin.* Trade name for the mercury salt of 2 : 6-diiodophenol-4-sulphonic acid. Used in skin diseases.

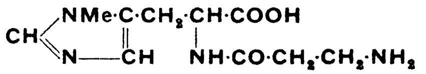
ANON. *Hexanon, Sexton.* Trade name for *cyclo*hexanone,



Solvent in cellulose ester varnishes.

ANORTHITE *v.* FELSPAR.

ANSERINE. *α-(β-alanyl)amino-β-*(N*-methyl-5-iminazolyl)-propionic acid,*



This base was discovered in goose muscle by Ackermann, Timpe, and Poller (Z. physiol. Chem. 1929, **183**, 1) and is the *N*-methyl derivative of carnosine. It has been found associated with carnosine in the muscle of the cat, dog, deer, gnu, opossum, rabbit and crocodile ; the muscle of the llama, crow, hen, pigeon, turkey, cod, conger-eel and dog-fish contains anserine but no carnosine, whereas there is only carnosine in the muscle of the horse, ox, river eel and boa constrictor (Ackermann, Timpe, and Poller, *l.c.* ; Hoppe-Seyler, Linneweh, and Linneweh, Z. physiol. Chem. 1929, **184**, 276 ; Ackermann and Hoppe-Seyler, *ibid.* 1931, **197**, 135 ; Wolff and Wilson J. Biol. Chem. 1932, **95**, 495 ; 1935, **109**, 565).

For details of the elucidation of the constitution of anserine, *see* Linneweh, Keil, and Hoppe-Seyler (Z. physiol. Chem. 1929, **183**, 11), Keil (*ibid.* 1930, **187**, 1), Linneweh and Linneweh (*ibid.* 1930, **189**, 80), and Pyman (J.C.S. 1930, 183). The base, m.p. 238°–239°, has $[a]_D^{16}$ in water +11·26°. *Nitrate*, m.p. 220°–222° (decomp.); *chloroplatinate*, m.p. 215°–220° (decomp.); *chloroaurate*, m.p. 90°–95°; *picrate*, m.p. 205°–208° (decomp.); *flavianate*, m.p. 200°–205°; *copper oxide*, $C_{10}H_{16}O_3N_4{\cdot}CuO$, m.p. 230°–232° (decomp.); *ethyl ester chloroplatinate*, m.p. 225°–230°. W. V. T.

ANTALGINE *v.* AGATHIN. Methylphenyl hydrazone of salicylaldehyde. Analgesic, antirheumatic.

ANTHEMIS NOBILIS (Fam. Compositæ). *Chamomile.* The essential oil distilled from the flowers has the following properties: sp.gr. 0·905–0·915; n_D^{20} 1·442–1·448; saponification value, 260–296; acid value, 1·5–14·0; soluble in 6 volumes of 70% alcohol (B.P.C. 1934, 684). The colour of the freshly distilled oil is due to chamazulene, a blue hydrocarbon, $C_{15}H_{18}$ (L. Ruzicka and E. A. Rudolph, A. 1926, 299), also found in oil of milfoil (*v.* ACHILLEA). The oil contains butyl and amyl esters of angelic and tiglic acids, an alcohol *anthemol*, $C_{10}H_{16}O$, *anthemene*, $C_{18}H_{36}$, m.p. 63°, and a monocyclic hydrocarbon $C_{15}H_{24}$ (A. 1928, 298). The oil is used in medicine as a carminative.

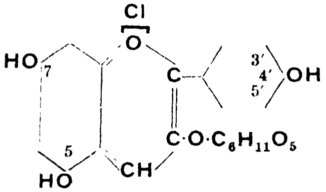
ANTHEMOL *v.* ANTHEMIS NOBILIS.

ANTHERAXANTHIN, $C_{40}H_{56}O_3$ or $C_{40}H_{58}O_3$, the carotenoid pigment from the pollen sacs of the tiger lily (*Lilium tigrinium*) (Karrer and Oswald, Helv. Chim. Acta, 1935, **18**, 1303), crystallises from ethyl alcohol in deep red leaflets, m.p. 207° (211° corr.), and resembles zeaxanthin in its solubilities in solvents and its hypophasic behaviour when partitioned between alcohol and light petroleum. Antheraxanthin shows absorption maxima in carbon disulphide at 512·5, 481, 448$m\mu$, in chloroform at 490·5, 460·5, 428$m\mu$. When an ethereal solution of the pigment is shaken with hydrochloric acid the acid layer turns first blue, then green (*v.* CAROTENOIDS). I. M. H. and R. F. P.

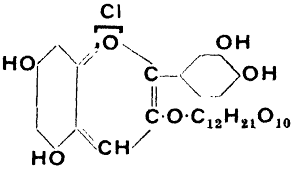
ANTHOCYANS. The anthocyan pigments occur naturally in flowers, fruit, leaves, etc., as the sap-soluble glycosidic *anthocyanins*, varying in colour from scarlet, magenta and purple to blue. Their sugar-free aglycones are termed *anthocyanidins*. Their amphoteric nature is shown *in vitro* by the formation of stable red oxonium salts when in combination with acid, violet or purple colour bases when in neutral solution and purple or blue phenolic salts when alkaline.

The isolation and identification of *cyanin* from the cornflower by Willstätter and Everest (Annalen, 1913, **401**, 193) was followed by the classical work on the isolations and analyses of these compounds by Willstätter's school (Annalen, 1915, **408**, and 1917, **412**) and their syntheses by Robinson and his collaborators (J.C.S., numerous papers since 1922); and by the contributions of Karrer's laboratory at Zürich (Helv. Chim. Acta, 1926, **10**, to 1932, **15**). Natural pigmentation may be due either to one or to a mixture of anthocyanins.

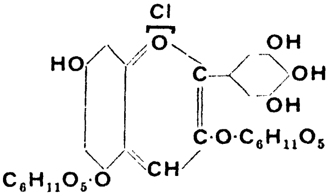
With a few exceptions the anthocyanins, which are flavylium salts, fall into three groups represented by the *pelargonidin*, *cyanidin*, and *delphinidin* types, differing from each other only by additional hydroxyl groups at 3′ and 5′. They are represented below as hydrochlorides, in which form they are most easily isolated and identified. Variations within the type are due to methylation at 3′, 5′, and 7, and to variation in the nature, number, and position of the molecules of sugar. One glycosidic residue is always present at 3. A few anthocyanins are acylated and have an organic acid incorporated in the molecule.



Pelargonidin 3-monoglycoside.



Cyanidin 3-bioside.



Delphinidin 3–5-diglycoside.

Rare types include the nitrogenous *betanin* group (Schudel, Dissertation, 1918, Zürich; Robinson and Robinson, J.C.S. 1932, 1439), *carajura* (Chapman, Perkin, and Robinson, J.C.S. 1927, 3015), gesnerin (Robinson and Robinson, Biochem. J. 1932, **26**, 1647), and the unidentified yellow pigment of *Papaver alpinum*, *Papaver nudicaule*, and *Meconopsis cambrica*.

Increasing knowledge of the chemistry of the anthocyanins has encouraged a return to the biochemical study of flower colour variation first attempted by Onslow (J. Genetics, 1914, **4**, 109; "The Anthocyanin Pigments of Plants," 1925). The distribution of the anthocyanins and leuco-anthocyanins and the blueing effect upon anthocyanins of certain anthoxanthin (flavone and flavonol) and tannin "co-pigments" have been studied over a large range of species and varieties by Robinson and Robinson (Biochem. J. 1931, **25**, 1687; 1932, **26**, 1647; 1933, **27**, 206; 1934, **28**, 1712; J.C.S. 1935, 744). The genetical aspect is being investigated by Lawrence and Scott-Moncrieff (J. Genetics, 1935, **30**, 155 ; 1936, **32**, 117), who maintain that a study of the biochemical effect of gene action should indicate the course of metabolism of the anthocyans and their relationships to the anthoxanthins.

Flower colour variation is largely due to the various changes in anthocyanin type outlined above, but co-pigmentation, change in the p_H of the cell sap, colloidal effects, pigment intensity, and the background effects of yellow plastid and anthoxanthin pigments also play a large part (*see* PLANT PIGMENTS). R. S.-M.

ANTHORINE *v.* ACONITINE AND ACONITE ALKALOIDS.

ANTHRACENE. Anthracene was discovered in 1832 by Dumas and Laurent as a constituent of the highest-boiling portions of coal-tar and was termed by them paranaphthalene (Annalen, 1833, **5**, 10) ; it was further examined by Laurent, who re-named it anthracene (Annalen, 1840, **34**, 287), and first obtained pure by Fritzsche (Annalen, 1859, **109**, 249) ; its properties were studied in greater detail by Anderson (Annalen, 1862, **122**, 294 ; J.C.S. Trans. 1862, **15**, 44). It was first synthesised in 1866 by Limpricht, who prepared it by heating benzyl chloride under pressure with water at 180°C.

For some time after its discovery anthracene remained a mere chemical curiosity and it was not until 1868, when Graebe and Liebermann obtained it by distilling alizarin over zinc dust, thus linking it with this important dyestuff, that the hydrocarbon became of any commercial importance. The synthesis of alizarin from an anthracene derivative followed in 1869 when the technical production of alizarin from anthraquinone sulphonic acid was patented by Caro, Graebe, and Liebermann and also independently by Perkin.

As a source of dyestuffs the demand for anthracene was at first considerably in excess of the supply and at one time the value of the anthracene recovered by the tar distiller was greater than the total value of his crude tar although the amount of anthracene obtained was considerably less than 1% of the tar. This demand for anthracene led to the evolution of a considerable number of processes for the production of anthracene by pyrolysis, *e.g.* from Caucasian petroleum (Letny, Ber. 1877, **10**, 412 ; 1878, **11**, 1210) ; lignite tar oil (Liebermann and Burg, Ber. 1878, **11**, 723) ; wood tar oil (Atterberg, Ber. 1878, **11**, 1222) ; Baku petroleum (Dingl. poly. J. 1883, **246**, 429) ; light petroleum vapour (Elliott, Amer. Chem. J. 1884, **6**, 248); and from the distillation of rhein with zinc dust (Oesterle and Tisza, Arch. Pharm. 1908, **432**). As the production of anthracene increased, the market price fell considerably and to-day coal-tar constitutes the main source of the hydrocarbon, its production from other sources being uneconomic and of historical interest only. Moreover, when the anthracene is derived from paraffinoid sources, it is much more difficult to obtain the hydrocarbon in the state of purity required for the manufacture of dyestuffs of good quality.

Preparation of Anthracene from Coal-tar.—(References : Auerbach, "Das Anthracen und seine Derivate" ; Kopp, Jahresber. 1878, 1187 ; Perkin, J. Soc. Arts, 1879, **27**, 572 ; Lunge, "Coal Tar and Ammonia," Gurney and Jackson, 1916). The amount of anthracene present in coal-tar is largely dependent on the origin of the tar. The carbonisation of coal in horizontal retorts produces a tar containing about 0·4% of anthracene, and in coke ovens, about 0·5%, whilst the tar produced by carbonisation in vertical retorts or in processes of low-temperature carbonisation contains so little anthracene as to make its recovery uneconomical. The methods given below are therefore concerned with tars of the former type only.

Anthracene is obtained from the "heavy oil" distillate of the tar distiller ; this at first is greenish-yellow in colour, but turns more brown by the action of the air, and becomes semi-solid on standing, owing to the separation of solid substances. It contains, amongst other substances, naphthalene, methylnaphthalene, anthracene, methylanthracene, phenanthrene, chrysene, carbazole and acridine, together with hydrides of anthracene and phenanthrene and other high-boiling liquids. When no further separation occurs the mass is subjected to filtration, either in a centrifugal machine or a filter press, first in the cold and finally at 40°C. (Gessert, Dingl. poly. J. 1870, **196**, 543) ; or it is filtered through strong linen bags and afterwards submitted to hydraulic pressure in a press so arranged that the plates can be heated with steam and the cake hot-pressed. A notable quantity of anthracene remains dissolved in the expressed oil, and especially in the portions separated when the temperature is raised; this is recovered by re-distilling and working up the product as just described. A hard yellowish-green cake is obtained containing 25–40% of anthracene.

Many methods have been proposed for the purification of this crude anthracene. The methods may be classified in two groups :

(1) Purification by selective solvents which preferentially dissolve impurities.

(2) Conversion of impurities into compounds more readily removable.

(1) *Purification by Selective Solvents.*—Formerly, crude anthracene was heated with low-boiling coal-tar oils, *e.g.* solvent naphtha, light creosote, etc., which dissolved certain of the impurities and gave a residue on filtration containing 40–50% of pure hydrocarbon. Sublimation of this product with steam at a temperature of 220°–240°C. gave a product of 50–60% purity, suitable for conversion into anthraquinone by oxidation. To-day the purification of the 25–40% product by treatment with low-boiling solvents has been superseded by methods based on the far greater solubility of the impurities in pyridine and quinoline bases (Chemische Fabriks-Aktiengesellschaft in Hamburg, G.P. 42053 ; Clark, Ind. Eng. Chem. 1919, **11**, 204). The crude anthracene is dissolved at 100°C. in 1½–2 times its weight of a dehydrated and rectified mixture of tar bases (pyridine and homologues) separated

from the light oil obtained in tar distillation (*cf.* G.P. 34947 and 36372), and the solution, on cooling, yields a crystalline separation of anthracene almost free from carbazole and its homologues. The patentees state that a 33% anthracene dissolved in 1·75 times its weight of pyridine bases yields on crystallisation an 82·5% anthracene, whilst when dissolved in twice its weight of a mixture of equal parts of pyridine bases and benzene it yields an 80% anthracene, and in twice its weight of a mixture of equal parts of benzene and aniline, a 75% anthracene. The recovery of the anthracene contained in the mother liquors offers no special difficulty.

Remy and Erhart (G.P. 38417, 1886) have proposed crystallisation from oleic acid as a means of purification of crude anthracene. The difficulty of recovering the anthracene contained in the mother liquors would seem, however, to deprive this method of technical importance.

McDonald Graham (Chem. News, 1876, **33**, 99, 168) has devised a method for recovering anthracene from the filtered oils used in its purification.

The Farbenfabriken vorm. Friedr. Baeyer & Co. (G.P. 68474 ; B.P. 5539, 1892 ; J.S.C.I. 1893, **12**, 439) employ liquid sulphur dioxide, which dissolves the impurities of crude anthracene but very little anthracene itself.

Another patent of the same firm (G.P. 78861 ; B.P. 7862, 1894 ; J.S.C.I. 1895, **14**, 361) recommends the use of acetone or other fatty ketones as purifying agents.

Wilton (B.P. 27559, 1898 ; G.P. 113291 ; J.S.C.I. 1900, **19**, 139) purifies crude anthracene by means of liquid (anhydrous) ammonia, which dissolves out most of the impurities but not the anthracene itself.

Luyten and Blumer (B.P. 14892, 1900 ; G.P. 141186 ; J.S.C.I. 1901, **20**, 796) state that when anthracene is purified by solvents such as naphtha, acetone, etc., the presence of tar oil in the crude anthracene is beneficial.

According to Tetralin G.m.b.H. (G.P. 389878, 1922), 100 parts of 45% anthracene dissolved at 90°C. in 200 parts of *cyclo*hexanol or *cyclo*hexanone yield on cooling 43 parts of 95% anthracene, and if the crude anthracene be first washed with tetralin it is claimed that 100% anthracene can be obtained. The treatment of crude anthracene with hydrogenated naphthalene and a reagent for removing carbazole, such as pyridine, is recorded by Deutsche Hydrierwerke (G.P. 472183, 1922).

The use of alkylated arylamines, *e.g.* mono- or dimethylaniline, as selective solvents is proposed by Michael (G.P. 377473, 1921). Improved methods of extraction with liquid sulphur dioxide are claimed by A.-G. für Chem. Ind. (B.P. 193802, 1922), whereby it is stated that very pure anthracene can be obtained.

A combination of liquid SO_2 and acetone is suggested by Elgersma (F.P. 722795). According to Downs (U.S.P. 1303639, 1919), when solutions of crude anthracene in coal-tar naphtha are exposed to the action of ultra-violet light, the anthracene is precipitated as para-anthracene, which after separation can be reconverted to anthracene by sublimation.

Rabek and Bojanowski (Przemysl Chem. 1929, **13**, 508) first treat the crude anthracene with primary tar oil, boiling at 150°–240°C., and then with pyridine bases.

Jaeger (Ind. Eng. Chem. 1928, **20**, 1330 ; U.S.P. 1693713, 1928) uses furfural and certain of its derivatives as solvents for the removal of phenanthrene and carbazole, leaving anthracene of 96% purity (*see also* U.S.P. 1879686, 1841895) ; Norton (U.S.P. 1764031, 1930) uses hydrogenated furfuryl alcohol as a solvent for these impurities.

Daniels (Selden Co., U.S.P. 1831059) uses *o*-dichlorobenzene and other halogenated aromatic hydrocarbons of the benzene series.

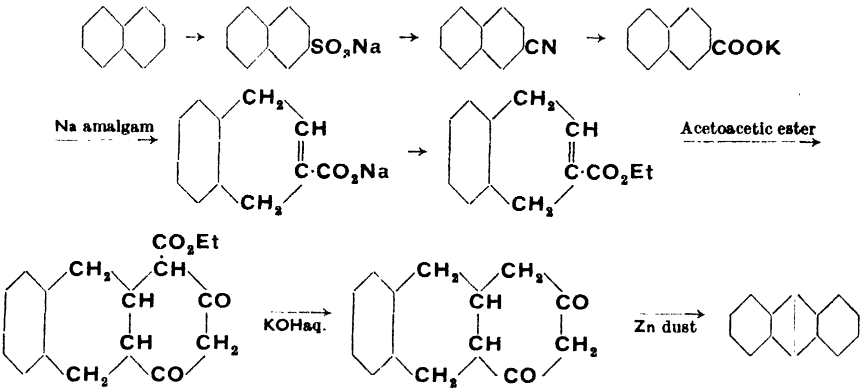
(2) *Conversion of Impurities into Compounds more readily Removable.*—Where the purity of the crude anthracene had formerly been increased to 50–60% by treatment with light coal-tar solvents followed by sublimation with steam, a further purification to remove carbazole and bodies of a phenolic character was effected by distillation with caustic potash (G.P. 111359, B.P. 7868, 1899 ; J.S.C.I. 1899, **18**, 750 ; F.P. 335013 ; J.S.C.I. 1904, **23**, 113 ; G.P. 178764 ; J.S.C.I. 1907, **26**, 1193). Kinzlberger (G.P. 374835, 1917) forms the potassium derivative of carbazole by treating a boiling solution of crude anthracene in solvent naphtha with 75% caustic potash solution. The potassium derivative separates as a solid, and 90% anthracene can be obtained from the solution ; according to Tetralin G.m.b.H. (G.P. 389878, 1922), a much purer anthracene (98–99%) may be obtained by this process if *cyclo*hexanol or *cyclo*hexanone be substituted for the naphtha as a solvent. Heating a pyridine solution of the anthracene with caustic potash is recommended by Kahl (B.P. 319762, 1928 ; G.P. 551028). Weil (B.P. 210742, 221999, 1923) distils crude anthracene in the vapour of petroleum hydrocarbons and passes the mixed vapours over caustic potash.

These methods of refining with caustic potash, on account of their cost, are not much used at the present day. Wirth (B.P. 14462, 1900 ; J.S.C.I. 1901, **20**, 464) separates the carbazole by means of its easily soluble nitroso-compound. Vesely and Votoček (B.P. 27596, 1904 ; J.S.C.I. 1905, **24**, 191) find that concentrated sulphuric acid extracts the whole of the basic impurities of anthracene from a solution of crude anthracene in a solvent immiscible with sulphuric acid. The most suitable solvents are mineral and coal-tar oils, but carbon disulphide and chloroform may be used ; 100 parts of crude anthracene (35%) are dissolved in 300 parts of refined solvent naphtha, 100 parts of concentrated sulphuric acid are added, and the mixture is heated and at the same time vigorously agitated for a few minutes. The sulphuric acid having been drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and then allowed to crystallise. By this process it is stated to be possible to obtain an 85–90% anthracene, perfectly free from carbazole.

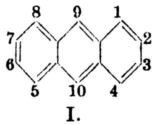
Maksorov (J. Chem. Ind. Moscow, 1929, 41) obtains pure anthracene by first removing phenanthrene with xylene and then separating the carbazole as a formaldehyde derivative.

Jaeger (B.P. 299419, 1927 ; Ind. Eng. Chem. 1928, **20**, 1330 ; U.S.P. 1920796, 1926540) removes the carbazole by passing the vapour of anthracene mixed with a limited amount of air over oxidising catalysts at 360°–430°C., whereby the carbazole is completely burnt to carbon dioxide and water. He suggests as suitable catalysts mixtures of titanium oxide, ferric oxide, copper oxide, nickel oxide, cobaltic oxide, etc., with potassium hydroxide.

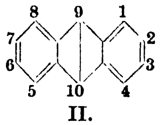
Synthesis.—Anthracene may be synthesised from liquid tolyl phenyl ketone by heating with zinc dust (Behr and Van Dorp, Ber. 1874, **7**, 17) ; from *o*-bromobenzyl bromide by the action of sodium (Jackson and White, Ber. 1879, **12**, 1965) ; from a mixture of benzene, acetylene tetrabromide and aluminium chloride (Anschütz, Annalen, 1886, **235**, 156) ; from benzene and aluminium chloride under the influence of nickel carbonyl at 100°C. (Dewar and Jones, J.C.S. Trans. 1904, **85**, 213) ; by treating pentachlorethane in benzene with aluminium chloride, when anthracene is formed through the intermediate formation of perchlorethylene (Mouneyrat, Bull. Soc. chim. 1898 [iii], **19**, 557) ; from benzyl trichloracetate by the action of aluminium chloride (Delacre, Compt. rend. 1895, **120**, 155) ; from diphenylmethane by means of aluminium chloride (Scholl and Seer, Ber. 1922, **55** [B], 335) ; from *o*-tolyl phenyl ketone by passage over active carbon at 380°–400°C. (I.G. Farbenind. A.-G., B.P. 251270, 253911, and 258553, 1925) ; and from naphthalene as indicated below (Colver and Noyes, J. Amer. Chem. Soc. 1921, **43**, 898).



Structure.—The formula for anthracene is sometimes written as I, with seven conjugated double bonds capable of oscillation (Auwers, Ber. 1920, **53** [B], 941 ; Barnett, "Anthracene and Anthraquinone," p. 19), and sometimes as II, with a bridged bond between the meso 9- and 10-carbon atoms. Shearer (Proc. Physical Soc. 1923, **35**, 81) and Challenor and Ingold (J.C.S. 1923, **123**, 2066) state that there is chemical and crystallographic evidence showing that the outer rings differ in fundamental respects from benzene rings, and that tautomeric change within each ring is affected by the rest of the molecule.



I.



II.

Bragg (J. Soc. Arts, 1923, **71**, 267) suggests as an explanation that the carbon atoms are arranged in different planes. Bergmann (Ber. 1929, **62** [B], 754) gives the formula for dihydroanthracene showing all the carbon atoms except 1-, 4-, 5-, and 8- lying in one plane, with 1- and 8- in a plane above and 4- and 5- in a plane below, thus explaining the formation of two isomeric mono-substitution products in the 9-position and three isomeric di-substitution products in the 9- and 10-positions, and he has constructed a model of the anthracene molecule showing the carbon atoms 1-, 8-, and 9- lying in an upper plane, 4-, 5-, and 10- in a lower plane, and the others in an intermediate plane ; he claims that this is in agreement with the results of X-ray analysis, and that it explains the formation of isomeric substitution products. Banerjee (Nature, 1930, **125**, 456), however, maintains that an arrangement of all the carbon atoms in one plane agrees with experimental and theoretical structure factors.

Physical and Chemical Properties.—Anthracene crystallises in glistening white scales showing a bluish-violet fluorescence which may be concealed if small quantities of yellow impurities are present. Anthracene coloured by traces of a yellow impurity (Fritzsche's chrysogen) may be bleached on exposure to sunlight, becoming again fluorescent, but under these conditions the hydrocarbon is converted into *paranthracene* (*dianthracene*), $(C_{14}H_{10})_2$, a modification which is much less soluble than anthracene and differs from the latter in chemical properties ; it is reconverted to ordinary anthracene on fusion (Fritzsche, J. pr. Chem. 1867 [i], **101**, 333 ; Graebe and Liebermann, Annalen, Suppl. 1833, **7**, 264 ; Schmidt, J. pr. Chem. 1874 [ii], **9**, 248 ; Luther and Weigert, Chem. Zentr. 1904, ii, 117 ; 1905, i, 1152). The fluorescence of anthracene and certain of its derivatives has been attributed by Liebermann to a particular molecular grouping (Ber. 1880, **13**, 913). Meyer (Z. physikal. Chem. 1897, **24**, 468) attributes fluorescence to the presence of what are known as fluorphoric groups, which must be situated between two heavy atomic groups such as benzene nuclei.

According to Dutt (J. Indian Chem. Soc. 1930, **7**, 505) the bluish' fluorescence associated with anthracene crystals is due to the presence of some impurity. By heating with water under pressure, followed by sublimation and crystallisation, he has been able to obtain non-fluorescent crystals. The fluorescence returned on exposure to air. (For a discussion of the fluorescence of anthracene, *see* Stevenson, J. Physical Chem. 1911, **15**, 845). Hibbert (J. Soc. Dyers and Col. 1928, **44**, 377) has shown that exposure to light promotes oxidation and she has been able to identify anthraquinone in portions of the crystals which have turned yellow. The photochemical polymerisation of anthracene has been investigated by Weigert (Naturwiss. 1927, **15**, 124).

Chrysogen, the name given to the yellow impurity in anthracene, has recently been isolated by Winterstein, Shon, and Vetter (Fuel, 1935, **14**, 187), who have identified it as naphthacene. They found that the presence of naphthacene to the extent of one part in three million parts was sufficient to destroy the blue fluorescence of anthracene.

Various figures have been given for the melting-point and boiling-point of pure anthracene: Kirby (J.S.C.I. 1921, **40**, 274T) gives the melting-point as 218°C. and the boiling-point as 340°C.; Nelson and Senseman (Ind. Eng. Chem. 1922, **14**, 58) give the boiling-point as 342°C.; International Critical Tables give the melting-point as 216·55°C. and the boiling-point as 342°C.

The solubility of anthracene in 100 parts of various solvents has been determined by Versmann (Jahresbericht, 1874, 423), Perkin (J. Soc. Arts, 1879, **27**, 598), v. Becchi (Ber. 1879, **12**, 1978), Findlay (J.C.S. 1902, **81**, 1217) with the following results:

	Parts of anthracene.
Alcohol (absolute) @ 16° dissolves	0·076 (B)
,, ,, @ b.p. ,, .	0·830 (B)
,, sp.gr. =0·800 @ 15° ,, .	0·591 (V)
,, ,, =0·825 ,, ,, .	0·574 (V)
,, ,, =0·830 ,, ,, .	0·491 (V)
,, ,, =0·835 ,, ,, .	0·475 (V)
,, ,, =0·840 ,, ,, .	0·460 (V)
,, ,, =0·850 ,, ,, .	0·423 (V)
Ether ,, ,, .	1·175 (V)
Chloroform ,, ,, .	1·736 (V)
Carbon disulphide ,, ,, .	1·478 (V)
Acetic acid ,, ,, .	0·444 (V)
Light petroleum ,, ,, .	0·394 (V)
,, ,, b.p. 70°–100°, @ 15° dissolves	0·115 (P)
Benzene @ 15° dissolves . . .	1·296 (F)
Benzole, b.p. 80°–100°, @ 15° dissolves	0·976 (P)
Toluene @ 16·5° dissolves . . .	0·920 (B)
,, @ b.p. ,, . . .	12·940 (B)

According to Hildebrand, Ellefson, and Beebe (J. Amer. Chem. Soc. 1917, **39**, 2301) the solubilities of anthracene at 25°C. in g. per 100 g. of the solvents are as follows:

Alcohol	0·328
Benzene	1·86
Carbon disulphide .	2·58
Carbon tetrachloride.	0·732
Ether	1·42
Hexane	0·37

When introduced into an alcoholic solution of picric acid saturated at 30°–40°C., anthracene forms a picrate, $C_{14}H_{10}{\cdot}C_6H_2(NO_2)_3OH$, crystallising in glistening red needles which melt at 138°C.; this picrate is decomposed into its constituents by alcohol, water or dilute alkalis, even in the cold.

Anthracene gives additive compounds with picramide and picryl chloride (Efremov, J. Russ. Phys. Chem. Soc. 1918, **50**, 421) and also a scarlet compound with trinitrobenzene (Sudborough, J.C.S. 1916, **109**, 1339).

Oxidation.—On oxidation with potassium dichromate or manganese dioxide and sulphuric acid, anthracene is converted into anthraquinone, whilst strong nitric acid oxidises it to anthraquinone and dinitroanthraquinone; nitro-derivatives of anthracene can, however, be prepared by the action of strong nitric acid on the hydrocarbon, if care is taken to decompose any nitrous acid which may be formed during the reaction (Perkin, Chem. Soc. Proc. 1889, 13). Electrolytic oxidation in acetone also yields anthraquinone (Fontana and Perkin, Chem. Zentr. 1904, ii, 708); the same product results by the electrolytic oxidation of a suspension of anthracene in a 2% solution of cerium sulphate in 20% sulphuric acid at 80°–90°C. (Farbw. vorm. Meister, Lucius u. Brüning, G.P. 152063; Chem. Zentr. 1904, ii, 71) or by the oxidation of anthracene by cerium oxide in sulphuric acid (Farbw. vorm. Meister, Lucius u. Brüning, G.P. 158609; Chem. Zentr. 1905, i, 840); or by passing the vapour of anthracene mixed with air over coal heated at 150°–300°C. (Dennstedt and Hassler, G.P. 203848; Chem. Zentr. 1908, ii, 1750).

Other oxidising methods are with potassium chlorate in the presence of an osmium salt (Hofmann, Ehrhart, and Schneider, Ber. 1912, **45**, 3334; 1913, **46**, 1669); with sodium nitrate or chlorate in the presence of molten crystallised magnesium chloride (Hofmann, Schneider, and Quoos, Ber. 1914, **47**, 1991; G.P. 277733); with aqueous sodium hypochlorite in the presence of a trace of an osmium salt at ordinary temperatures (Hofmann and Ritter, Ber. 1914, **47**, 2238). Methods of oxidation by nitric acid and oxides of nitrogen have been patented (G.P. 284179, 268049, 234289, 254710). Oxidation has also been attempted with oxygen (G.P. 292681; B.P. 134522; G.P. 578723) and with ozone (B.P. 5514, 1915).

The older methods of oxidising anthracene to anthraquinone are now being rapidly superseded by the air oxidation process operating at a temperature of 180°–280°C. and using as catalysts vanadates, chromates, or molybdates of silver, lead, nickel, cobalt, etc. (Wohl, G.P. 349089, 1916), or at 360°–450°C. using zeolitic material containing vanadium or ferric oxide (Jaeger, U.S.P. 1685635, 1844395). The use of a protective vapour such as carbon tetrachloride for moderating the rise and fall in temperature of the mixture has also been protected (Jaeger, U.S.P. 1909355). Oxidation by moist carbon dioxide in the presence of a vanadium catalyst has also been suggested (Badische, G.P. Appl. B. **96**, 137). Iljinski and Maksorov (Z. Farbenind. 1929, **20**, 210, 244) use nitric oxide as an oxidant.

Sulphonation.—Concentrated sulphuric acid converts anthracene into sulphonic acids. Anthracene mono-sulphonic acid is obtained by the direct sulphonation of anthracene with sulphuric acid of 53° or 54°B. and about 60% of the anthracene employed is thus converted. If sulphuric acid of 66°B. is used, two isomeric disulphonic acids are obtained, and these, on oxidation, yield two anthraquinone disulphonic acids, which are isomeric with the two acids obtained by the direct sulphonation of anthraquinone. The β-anthracene disulphonic acid, after oxidation with chromic or nitric acids and subsequent fusion with alkali, yields alizarin (*q.v.*). The monosulphonic acid similarly treated yields anthrapurpurin (*q.v.*) (La Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, B.P. 1280, 1893 ; J.S.C.I. 1894, 32). The same acids are obtained by heating anthracene with alkali bisulphate to 140°–150°C. (G.P. 77311). Sulphonation by chlorsulphonic acid in glacial acetic acid solution at 95°C. has been patented by Bayer & Co. (G.P. 251695).

Halogenation.—Anthracene is readily attacked by chlorine and bromine, and yields with each element a series of additive and substitution derivatives ; additive compounds, apparently, are the first products of the action, and these either decompose during the reaction or can be decomposed by boiling with alcoholic potash into the corresponding substitution derivatives, which also form additive compounds by the further action of the halogens. These may again lose halogen acid, substitution taking place in the benzene rings. The method adopted by the Clayton Aniline Co. (B.P. 8744, 1905 ; J.S.C.I. 1906, 64) for the preparation of the chloranthracenes is as follows. Dry chlorine reacts with anthracene in the presence of lead peroxide at a high temperature. Fifty parts by weight of anthracene and 10 parts of dry powdered lead peroxide are treated with dry chlorine at 220°C. until the weight has increased to 120 parts. The temperature, however, may be varied between 180°–260°C. and the composition of the product varies with the temperature employed and the amount of chlorine absorbed. The product consists mainly of β-tetrachloranthracene (m.p. 152°C.), which is readily soluble in benzene and crystallises out in yellow needles, and of another portion much less soluble in benzene and more highly chlorinated. This latter consists of two products: hexachloranthracene (m.p. 277°), which crystallises from nitrobenzene, and heptachloranthracene (m.p. 232°), which is more soluble in benzene than the former. Chlorine derivatives of anthracene have also been prepared by heating anthraquinone with a mixture of phosphorus pentachloride and oxychloride (Graebe and Liebermann, Annalen, 1871, **160**, 126 ; Radulescu, Chem. Zentr. 1908, ii, 1032).

Hydrogenation.—Reducing agents such as sodium amalgam or phosphorus and hydrogen iodide convert anthracene into the dihydride (Liebermann and Topf, Annalen, 1882, **212**, 5) ; hydrogen and nickel oxide at 260°–270°C. and 100–125 atm. convert anthracene first into tetrahydro-, then decahydro-, and finally perhydroanthracene (Ipatieff, Jakowleff and Rakitin, Ber. 1908, **41**, 996). Schroeter (Ber. 1924, **57** [B], 2003) and Braun and Bayer (Ber. 1925, **58** [B], 2667) have examined the hydrogenation of anthracene under pressure and find that two hydrogen atoms are first added in the meso-positions followed by two more in the side rings. The third phase involves the shifting of the two meso-hydrogen atoms to the side ring, the centre ring becoming aromatic and all four additional hydrogen atoms being found attached to one side ring. Finally, octahydroanthracene is produced with four more hydrogen atoms in the other side ring. For more recent work on the hydrogenation of anthracene, reference should be made to papers by Fries, Schilling, and Littmann (Ber. 1932, **65** [B], 1494–1502) ; Kagehira (Bull. Chem. Soc. Japan, 1931, **6**, 241–54) ; Kling and Florentin (Compt. rend. 1931, **193**, 1198) ; Hügel and Friess (Ann. combustible liquides, 1931, **6**, 1109–47 ; 1932, **7**, 39–96) ; Martin and Hügel (Bull. Soc. chim. 1933 [iv], **53**, 1500–02).

Estimation.—(Luck, Ber. 1873, **6**, 1347 ; Meister, Lucius, and Brüning, Dingl. poly. J. 1877, **224**, 559 ; Nicol, J.C.S. Trans. 1876, **2**, 553 ; Bassett, Chem. News, 1896, **73**, 178 ; 1899, **79**, 157.) The percentage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone with chromic acid, dissolving the product in sulphuric acid, and precipitating with water; the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water. The details of the Höchst process are as follows : 1 g. of anthracene is introduced with 45 c.c. of acetic acid into a flask connected with a reflux condenser, and heated to boiling. A solution of 15 g. of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added, drop by drop, to the boiling solution during a period of 2 hours, the product boiled for 2 hours longer, allowed to stand for 12 hours, then poured into 400 c.c. of water and, after standing for 3 hours longer, is filtered. The anthraquinone on the filter is washed with water, with hot dilute alkali, and then with hot water ; afterwards it is placed in a small dish dried at 100°C., and digested for 10 minutes with 10 times its weight of pure concentrated sulphuric acid at 100°C. The solution of anthraquinone in sulphuric acid is then allowed to remain for 12 hours in a moist atmosphere, mixed with 200 c.c. of water, and the precipitated anthraquinone filtered off and washed first with water, then with dilute alkali, and finally with water ; it is then dried at 100°C. in a dish, weighed, ignited, and the ash deducted from the first weighing. The difference gives the weight of anthraquinone corresponding to the amount of anthracene present in the sample (Meister, Lucius, and Brüning, Z. anal. Chem. 1877, **16**, 61).

As this method for the estimation of anthracene requires a considerable time (from 2–3 days) various modifications to shorten the method have been introduced (Rhodes, Nichols, and Morse, Ind. Eng. Chem. 1925, **17**, 839 ; Jacobsohn, Chem.-Ztg. 1926, **50**, 545 ; Pirak, Z. angew. Chem. 1928, **41**, 231). Sielisch (Z. angew. Chem. 1926, **39**, 1248) uses the Rütger method, which avoids the sulphonation treatment required by the Höchst method by reducing the anthraquinone with alkali hydrosulphite solution to hydroanthraquinone, thus bringing it into solution. After filtration the anthraquinone is regenerated from the solution by oxidation with air or hydrogen peroxide. It is stated that this method requires only 3–3½ hours.

Jacobsohn and others recommend the use of Jena glass filtering crucibles in this estimation. Pavolini (Industria Chimica, 1930, 862) estimates phenanthrene in crude anthracene by means of the monoxime of phenanthraquinone which gives a cochineal-coloured precipitate with cobaltic chloride.

Paraffin is usually present in crude anthracene, and is estimated by treating the material with fuming nitric acid, keeping the mass cold. When all the acid has been added, the mixture is kept at ordinary temperature until the anthracene has dissolved, and then heated until the paraffin has melted. The solution is cooled, filtered through asbestos, and the precipitate washed with fuming nitric acid until the filtrate dissolves in water without turbidity, and then washed with water until neutral. Finally, the paraffin is washed with alcohol, dissolved in warm ether, and the filtrates collected in a weighed porcelain dish, evaporated and the paraffin dried for half an hour at 105°–110°C. (Heusler and Herde, J.S.C.I. 1895, **14**, 828). Kraemer and Spilker (Muspratt-Bunte, vii, 70) use the following method : 10 g. of the finely powdered anthracene is shaken with 100 c.c. of ether for ten minutes and the mixture then allowed to settle ; 50 c.c. of the clear solution is then evaporated and the residue dried at 100°C. for half an hour. After cooling, the residue is finely ground, 8 c.c. of fuming sulphuric acid (20% SO_3) added, well mixed, and the whole heated to 100°C. for three hours with frequent stirring. The contents of the dish are then washed by means of 500 c.c. of hot water into a beaker, filtered through a dry filter, and the whole washed with cold water until the filtrate is free from sulphuric acid. The filter is moistened with absolute alcohol and the paraffin washed into a weighed dish by means of ether, the last traces of paraffin being removed from the beaker in the same manner. The ether solutions are evaporated and the residue dried for half an hour at 105°C. ; the pure paraffin is then weighed.

The presence of carbazole in a sample of anthracene may be detected by extracting in the cold with ethyl acetate, allowing the solution to evaporate and transferring the residue by a few drops of the same solvent to a watch-glass. On evaporation carbazole is left behind ; when treated with nitrobenzene and a little phenanthraquinone, it yields characteristic small copper-coloured plates. Phenanthrene, if present, may be detected by extracting the sample with benzene, evaporating the solution, and treating the residue with α-dinitrophenanthraquinone in nitrobenzene. In this case mixed crystals are obtained having the form and colour of the brown needles of the phenanthrene compound, but containing a large quantity of anthracene. E. V. E.

ANTHRA YELLOW R *v.* ANTHRAQUINONE DYESTUFFS.

ANTHRACENE BLUE *v.* ALIZARIN AND ALLIED DYESTUFFS.

ANTHRACENE OIL *v.* ACRIDINE.

ANTHRACHROME DYESTUFFS. Dyestuffs, Azo mordant.

ANTHRACHRYSON (ANTHRACHRYSAZIN) *v.* ALIZARIN AND ALLIED DYESTUFFS.

ANTHRAFLAVIN (ANTHRAFLAVIC ACID) *v.* ALIZARIN AND ALLIED DYESTUFFS.

ANTHRAFLAVONE G *v.* ANTHRAQUINONE DYESTUFFS.

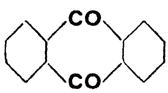
ANTHRAGALLOL *v.* ALIZARIN AND ALLIED DYESTUFFS.

ANTHRALAN COLOURS *v.* ANTHRAQUINONE DYESTUFFS.

ANTHRANOL *v.* ANTHRONE AND THE ALLIED COMPOUNDS.

ANTHANTHRONE *v.* ANTHRAQUINONE DYESTUFFS.

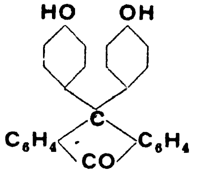
ANTHRAQUINONE,

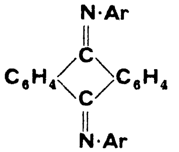


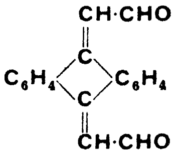
Anthraquinone is obtained industrially both by the oxidation of anthracene and by synthesis from phthalic anhydride and benzene. For details of these methods, *see* article ALIZARIN AND ALLIED DYESTUFFS.

Anthraquinone is a pale yellow compound which crystallises and sublimes in needles melting at 280°. Although it contains two *para* keto groups it does not behave as a benzenoid or true quinone inasmuch as it is not reduced by sulphites and it does not react with phenylhydrazine. It forms a monoxime but only with difficulty since it must be heated to 180° with hydroxylamine hydrochloride before reaction takes place. No dioxime is known. The monoxime and monophenylhydrazone can be easily obtained, however, by the reaction of hydroxylamine hydrochloride and phenylhydrazine respectively upon *meso*-dibromanthrone.

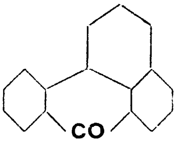
Anthraquinone condenses at high temperatures with phenols, primary aryl-amines and with aldehyde-ammonia to give compounds of the following types :





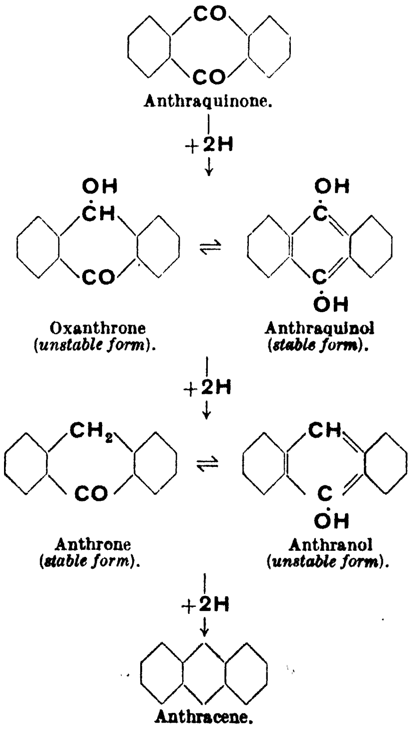


With glycerol and sulphuric acid it forms the industrially important benzanthrone and it reacts normally with Grignard compounds, first one and then the other keto group undergoing condensation.



Benzanthrone.

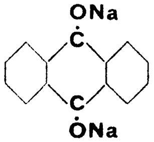
On reduction anthraquinone yields anthracene but intermediate reduction products which exhibit trans-annular keto-enol tautomerism can be isolated with ease. The relationship between these and the parent compound is shown by the following scheme :



When anthraquinone is boiled with a mixture of zinc dust and ammonia it gradually dissolves, with production of an intense red colour, due to the formation of the alkali-soluble anthraquinol. If this red solution is cooled and quickly filtered and then acidified with dilute hydrochloric acid in an atmosphere of carbon dioxide anthraquinol is precipitated as a yellow powder, m.p. 180°. It is the enol-desmotrope of oxanthrone and is very unstable since it oxidises to anthraquinone in the air even in the dry state.

Prolonged treatment of anthraquinone with zinc dust and ammonia at the boiling-point yields anthracene and this is the standard laboratory method of reducing an anthraquinone derivative to the corresponding anthracene derivative. When halogen substituents are present, however, there is risk of them being removed especially if they occupy α-positions.

Sodium hyposulphite reacts with an alcoholic solution of anthraquinone to form anthraquinol, but when anthraquinone is treated with an aqueous caustic alkaline solution of sodium hyposulphite the soluble disodio-derivative of anthraquinol is obtained. The same reaction takes place with all substituted anthraquinones, the soluble alkali derivative of the corresponding anthraquinol being produced ; the latter is termed the "leuco compound" or the "vat" of the former. This reaction is of great importance to dyers, since it enables an insoluble anthraquinonoid vat dyestuff to be applied evenly to a fabric. The fabric to be dyed is passed through a bath of "vat" containing a solution of the dyestuff in aqueous caustic soda and sodium hyposulphite, squeezed between a pair of rollers, and then passed through a solution of sodium dichromate in dilute sulphuric acid when the leuco compound with which the material is now evenly impregnated is oxidised to the original dyestuff with production of the desired colour.

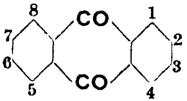


Disodio anthraquinol.

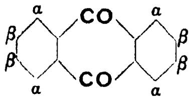
Oxanthrone, the unstable keto form of anthraquinol, is prepared free from anthraquinone by the oxidising action of bromine on an aqueous-acetone suspension of anthracene. It is a colourless compound, m.p. 167°, insoluble in caustic soda, but on boiling with strong alkali, however, it gradually enolises and passes into solution as the disodio derivative of anthraquinol.

Acid reducing agents on the other hand reduce anthraquinone directly to anthrone. Thus the action of strong hydrochloric acid and tin or iron borings upon a boiling aqueous suspension of anthraquinone, or the action of aluminium powder upon a sulphuric acid solution of anthraquinone at 30°–40° gives anthrone as the first product ; in the latter case the yield is about 90% of the theoretical. By the hydrogenation of anthraquinone in the presence of nickel, anthrone can be obtained in almost theoretical yield. Anthrone is insoluble in dilute caustic alkalis, but when boiled with strong aqueous alkalis it gradually enolises and dissolves as the sodio-derivative of anthranol from which the latter is on acidification precipitated as a golden powder.

The positions of substituents in anthraquinone derivatives are indicated by figures as in I or, usually only in monosubstituted derivatives, by the Greek letters as in II :



I.



II.

THE SULPHONIC ACIDS OF ANTHRAQUINONE.

For the direct sulphonation of anthraquinone, *see* ALIZARIN AND ALLIED DYESTUFFS.

Sulphonic groups can also be introduced into the anthraquinone nucleus by the replacement of nitro groups, by treatment of aminoanthraquinones with sodium hydrogen sulphite and by the addition of sulphites to 1:4-dihydroxyanthraquinones.

When α-nitroanthraquinone is heated under pressure with aqueous sodium sulphite replacement of the nitro group takes place with production of sodium anthraquinone-1-sulphonate. This replacement reaction takes place with greatest ease when the nitro compound is water-soluble, *e.g.* the nitroanthraquinone sulphonates, in which case boiling with sodium sulphite solution for half an hour in the open atmosphere is sufficient to effect quantitative replacement.

When 1:5-dinitro-4:8-dihydroxyanthraquinone is heated with aqueous sodium hydrogen sulphite reduction of the nitro groups and simultaneous sulphonation of the nucleus takes place with production of sodium 1:5-diamino-4:8-dihydroxyanthraquinone-2:6-disulphonate (Alizarin Saphirol B).

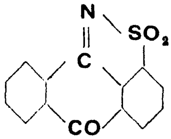
Quinizarin, on treatment with boiling aqueous sodium sulphite, yields quinizarin-2-sulphonic acid. A few other 1:4-disubstituted anthraquinones are sulphonated in the 1:4-substituted nucleus by this remarkable addition of sulphites.

Properties, Reactions, and Identification of Anthraquinone Sulphonic Acids.—The mono- and disulphonic acids of anthraquinone are strongly acidic substances of ill-defined melting-points which invariably appear in commerce in the form of their yellow sodium salts. Sodium anthraquinone-2-sulphonate is known technically as "silver salt." In view of the ease with which the sulphonic acids of anthraquinone can be obtained in a state of high purity, *i.e.* freedom from isomers, and because of the facility with which the sulphonic groups can be replaced by other radicles such as hydroxyl, amino, chlorine, etc., these compounds occupy a position of high technical importance as initial materials for the preparation of the valuable series of anthraquinonoid substantive and vat dyestuffs of great colour permanence. These important replacement reactions are described under the appropriate section.

The sulphonyl chlorides of anthraquinone are obtained by treating the anhydrous finely divided sodium sulphonates with phosphorus pentachloride in boiling phosphorus oxychloride solution. The latter is removed by distillation and the residue then washed with water, dried, and recrystallised from a suitable solvent. The mono- and disulphonyl chlorides are very stable towards water and can be boiled in aqueous suspension for several hours without undergoing appreciable decomposition. They are rapidly hydrolysed, however, by hot caustic alkalis. The α- and β-monosulphonyl chlorides crystallise from benzene in pale yellow plates, m.p. 214° and 197° respectively, and are satisfactory compounds for identifying the parent sodium sulphonates. The six disulphonyl chlorides are almost insoluble in benzene but crystallise well from nitrobenzene ; they have, however, ill-defined melting-points and are consequently of little value for reference purposes.

Chlorosulphonic acid reacts with β-sulpho groups to give the corresponding β-sulphonyl chlorides in good yield, but it has no action upon α-sulpho groups.

The α- and β-monosulphonyl chlorides react differently with ammonia : the latter yields the straightforward anthraquinone-2-sulphonamide, whereas the former gives the anhydride,



By heating the α-monosulphonate or the 1:5- or 1:8-disulphonates with aliphatic mercaptans in alkaline aqueous solution the sulpho groups are replaced with the production of anthraquinone thio-ether, thio-ether sulphonates and dithio-ethers. The reaction takes place with great ease at 100° and provided the right concentrations are employed the product separates after a few minutes. With the 1:5-disulphonate the intermediate sodium 1-thio-ether anthraquinone-5-sulphonate can be obtained in fairly good yield owing to its low solubility, but this is not the case with the 1:8-isomer the high solubility of which favours the direct formation of the dithio-ether. Sulpho groups in the β-positions are not attacked by alkaline mercaptans and upon this fact is based an important industrial method for determining the amount of sodium anthraquinone-1-sulphonate in "silver salt."

Treatment of the 1-thio-ether and the 1:5- and 1:8-dithio-ethers with fuming nitric acid at the boiling-point converts them into the corresponding sulphones according to the equation:

$$C_{14}H_7O_2{\cdot}S{\cdot}C_2H_5 \rightarrow C_{14}H_7O_2{\cdot}SO_2{\cdot}C_2H_5$$

The monosulphonates and the αα- and αβ-disulphonates of anthraquinone are most readily identified by converting them into the corresponding mono- or dichloroanthraquinones by treatment with aqueous nascent chlorine; the reaction takes place with great ease and the products are all well-defined substances possessing sharp melting-points. In the case of the 2:6- and 2:7-disulphonates the products of chlorination are the insoluble sodium 2-chloroanthraquinone-6- and -7-sulphonates which are easily identified by conversion into the corresponding chloroanthraquinone sulphonyl chlorides, m.p. 203° and 201° respectively.

Treatment of anthraquinone α-mono- and αα-disulphonates with aqueous potassium methylate causes replacement of the sulpho groups with formation of the α-mono- and αα-dimethylethers of anthraquinone; with potassium phenate the corresponding α-phenoxy- and αα-diphenoxyanthraquinones are obtained. For the replacement of β-sulphonic groups by methoxyl exclusion of water is necessary.

Sulphonic groups attached to the anthraquinone nucleus can frequently be removed by hydrolysis and replaced by hydrogen. Heating with concentrated sulphuric acid for 8 hours at 200° will completely hydrolyse an α- or two α-sulpho groups but will not affect the β-sulpho group or groups. The presence of hydroxyl groups in the same nucleus as a β-sulpho group, however, frequently confers mobility upon the latter rendering it easily removable under these conditions; for example, sodium alizarin-3:5- and -3:8-disulphonates give good yields of sodium alizarin-5- and -8-monosulphonates respectively. A mixture of the latter monosulphonates of alizarin finds application as a dyestuff under the name of *Eweco Acid Alizarin Red* SB. Sometimes sulphonic groups can be removed by the action of reducing agents.

The disulphonic acids of anthraquinone are very stable systems which cannot be nitrated or further sulphonated; treatment with high-concentration oleum merely leads to hydroxylation of the nucleus.

Sulphonation of Hydroxyanthraquinones.—The hydroxyanthraquinones are no less resistant to sulphonation than is anthraquinone itself but the hydroxyl groups exert a powerful orienting influence upon the entering sulpho radicle directing it into a β-position which is adjacent to a hydroxyl group. The following are obtained by direct sulphonation of the parent hydroxyanthraquinone:

Erythroxyanthraquinone - 2 - monosulphonic acid and -2:4-disulphonic acid.

Alizarin-3-monosulphonic acid and -3:6- and -3:7-disulphonic acids.

Anthraflavin-3:7-disulphonic acid.

*iso*Anthraflavin-3:6-disulphonic acid.

Anthrarufin-2:6-disulphonic acid and -2:4:6:8-tetrasulphonic acid.

Chrysazin-2:7-disulphonic acid and -2:4:5:7-tetrasulphonic acid.

Purpurin-3-monosulphonic acid.

The β-directive influence of hydroxyl is stronger than the α-directive influence of mercuric salts but it acts *only in the hydroxyl-substituted nucleus*; thus, in the absence of mercuric oxide, alizarin yields the -3:6- and -3:7-disulphonic acids, while in its presence alizarin -3:5- and -3:8-disulphonic acids are obtained.

The addition of sulphites to quinizarin and its derivatives such as purpurin and quinalizarin is remarkable; these compounds on boiling with aqueous sodium sulphite are sulphonated in the β-position in the nucleus bearing the 1:4-dihydroxyl groups (*v.* ALIZARIN AND ALLIED DYESTUFFS).

Sulphonation of Chloroanthraquinones.—In contrast with the hydroxyanthraquinones, in which the substituted nucleus is first attacked, the two monochloroanthraquinones and the four homonuclear dichloroanthraquinones are first sulphonated in the unsubstituted nucleus.

α-Chloroanthraquinone yields a mixture of almost equal quantities of 1-chloroanthraquinone-6- and -7-monosulphonic acids which admit of rapid separation since the sodium salt of the former is very insoluble while that of the latter is easily soluble in water. Further sulphonation of these separately gives rise to sodium 1-chloroanthraquinone-2:6- and -4:6-disulphonates from the former, and sodium 1-chloroanthraquinone-2:7-disulphonate from the latter.

Sulphonation of α-chloroanthraquinone in the presence of mercury yields first 1-chloroanthraquinone-5-sulphonic acid and finally a mixture of 1-chloroanthraquinone-2:5- and -4:5-disulphonic acids. It is evident that the combined β-orienting influences of the carbonyl and the chlorine substituent are as powerful as the α-directing influence of the mercury catalyst.

Sulphonation of sodium 2-chloroanthraquinone -6- and -7-sulphonates (*v. infra*) gives rise respectively to sodium 2-chloroanthraquinone-3:6- and -3:7-disulphonates.

The following are produced by sulphonation of the parent dichloroanthraquinone in the presence or absence of mercury:

1:2-dichloroanthraquinone-6- and -7-sulphonic acids.

1:3-dichloroanthraquinone-6- and -7-sulphonic acids.

1:4-dichloroanthraquinone-6-sulphonic acid.

1:4-dichloroanthraquinone-5-sulphonic acid (+Hg).

2:3-dichloroanthraquinone-6-sulphonic acid.

2:3-dichloroanthraquinone-5-sulphonic acid (+Hg).

1:5-dichloroanthraquinone-2- and -4-sulphonic acid.

1:5-dichloroanthraquinone-4-monosulphonic and -4:8-disulphonic acids (+Hg).

1:8-dichloroanthraquinone-4-sulphonic acid and -4:5-disulphonic acid.

2:6 - dichloroanthraquinone - 3:7 - disulphonic acid.

2:7-dichloroanthraquinone-3-sulphonic acid.

The sodium chloroanthraquinone mono- and disulphonates are all pale yellow compounds possessing solubilities in water which are sufficiently different to allow of separation by fractional crystallisation of the isomers produced in the above reactions.

NITRATION OF ANTHRAQUINONE AND ITS DERIVATIVES.

Anthraquinone nitrates with great ease when it is treated in sulphuric acid solution with finely divided sodium nitrate or fuming nitric acid yielding 1-nitroanthraquinone, m.p. 228° ; no 2-nitroanthraquinone is formed during the reaction. The latter may be prepared by the diazo reaction from 2-aminoanthraquinone or by nitration of 2-aminoanthraquinone and deamidation of the resulting 3-nitro-2-aminoanthraquinone, or by the convenient method of directly oxidising 2-aminoanthraquinone with ammonium persulphate. Prolonged nitration of anthraquinone yields a complex mixture of dinitro-compounds. The nitrating agent attacks the α-positions much more readily than the β-positions the chief products being 1:5- and 1:8-dinitroanthraquinone, m.p. 422° and 312° respectively, the former predominating ; small quantities of 1:6- and 1:7-dinitroanthraquinones (about 5–10% each), m.p. 256° and 293° respectively, are simultaneously produced.

Nitration of 2-methylanthraquinone similarly yields 1-nitro-2-methylanthraquinone and finally a mixture of 1:5-dinitro-2-methyl- and 1:8-dinitro-2-methylanthraquinone, the former predominating.

Nitro groups in the α-positions are very reactive and undergo a series of important replacement reactions. Treatment of the nitro compound in sulphuric acid solution with chlorine causes replacement of the nitro group by chlorine, and by heating the nitro-compound with aqueous pyridine the nitro group is replaced by hydroxyl. Primary and secondary aliphatic amines and primary arylamines react readily to give the corresponding substituted aminoanthraquinones, according to the equation :

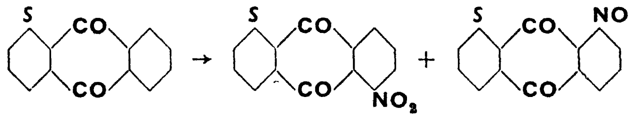
$$C_{14}H_7O_2{\cdot}NO_2+RNH_2 \rightarrow C_{14}H_7O_2{\cdot}NHR$$

The action of aqueous sodium sulphite at the boiling-point effects replacement of the nitro group by the sulphonic group (*v. supra*).

Both α- and β-nitro groups are replaced by methoxyl when the nitroanthraquinone is heated with methyl alcoholic potassium hydroxide and in this reaction it is to be noted that β-nitro groups are more reactive than α-groups.

1-nitro-2-methylanthraquinone is an important intermediate in the preparation of a series of valuable vat dyestuffs of the acridone and thioxanthone type (*v. infra*). Treatment with chlorine in sulphuric acid solution causes replacement of the nitro group by this element with simultaneous oxidation of the methyl group producing 1-chloroanthraquinone-2-carboxylic acid (*cf.* the formation of anthranilic acid from *o*-nitrotoluene). When 1-nitro-2-methylanthraquinone is heated with alcoholic potassium hydroxide intramolecular rearrangement takes place between the groups forming 1-aminoanthraquinone-2-carboxylic acid, which may also be prepared by the reduction of 1-nitroanthraquinone-2-carboxylic acid obtained by the oxidation of 1-nitro-2-methylanthraquinone with chromic acid in nitric acid solution. Reduction of 1-nitro-2-methylanthraquinone with sodium sulphide gives 1-amino-2-methylanthraquinone which on chlorination yields 1-amino-2-methyl-4-chloroanthraquinone.

Nitration of Anthraquinone Sulphonic Acids.—The two monosulphonic acids of anthraquinone are readily nitrated when their sodium salts are treated in sulphuric acid solution with fuming nitric acid. In each case both the α-positions in the unsubstituted nucleus are attacked giving rise to 1-nitroanthraquinone-5- and -8-sulphonic acids from the α-sulphonate and 1-nitroanthraquinone-6- and -7-sulphonic acids from the β-sulphonate, *e.g.* :



(Less soluble.) (More soluble.)

[S=$\cdot SO_3Na$]

The sodium nitroanthraquinone sulphonates are bright yellow crystalline substances possessing solubilities in water sufficiently different to allow of easy and almost complete separation of the isomers in each reaction.

On boiling the nitro-sulphonates with aqueous sodium sulphite the nitro group is quantitatively replaced by a sulphonic group with the production of the corresponding sodium anthraquinone disulphonate. This reaction provides the easiest laboratory method for the preparation of small quantities of the 1:6- and 1:7-disulphonates and derivatives directly obtainable from them. Treatment of the nitrosulphonates in aqueous solution with nascent chlorine yields the corresponding heteronuclear nitrochloroanthraquinones, which are thrown down as microcrystalline flocculent precipitates. These on reduction with aqueous sodium sulphide give the corresponding aminochloroanthraquinones. Homonuclear nitrochloro- and aminochloro-anthraquinones are prepared by other methods (*v. infra*).

The action of oleum on nitroanthraquinones does not yield nitroanthraquinone sulphonic acids but replacement of the nitro group by hydroxyl takes place accompanied by simultaneous sulphonation and hydroxylation of the nucleus. The reaction is exceedingly complex since hydroxylamino-, nitroso-, and quinonimido-compounds may be isolated by suitable means. In this manner 1:5- and 1:8-dinitroanthraquinones yield 1:3:4:5:7:8-hexahydroxyanthraquinone-2:6-disulphonate (*Anthracene Blue SWX*) and 1:3:4:5:6:8-hexahydroxyanthraquinone-2:7-disulphonate (*Alizarin Cyanine WRS*) respectively. By heating these compounds with dilute sulphuric acid the sulphonic groups are readily split off with production of 1:3:4:5:7:8-hexahydroxyanthraquinone (*Anthracene Blue WR*) and 1:3:4:5:6:8-hexahydroxyanthraquinone (*Alizarin Hexacyanine*).

Nitration of Aminoanthraquinones.—The aminoanthraquinones are sufficiently stable to be directly nitrated, but the constitution of the products depends very largely upon the conditions existing during the reaction. Frequently nitro-nitraminoanthraquinones are formed but the **N**-nitro group is very easily removed by hydrolysis. By direct nitration α-aminoanthraquinone yields 1-amino-2:4-dinitroanthraquinone whereas β-aminoanthraquinone gives 2-amino-3-nitroanthraquinone.

The amino group, however, is more usually protected by converting it into the alkyl, dialkyl-, acetyl-alkyl-, phthalimino-, urethane or oxamino-derivative, since the presence of the **N**-substituent exerts a definite directive influence upon the entering nitro group. By selecting the protective grouping a variety of nitroaminoanthraquinones may be obtained; thus 1-acetylaminoanthraquinone gives 1-acetylamino-4-nitroanthraquinone, while 1-acetylalkylaminoanthraquinone yields the 5-nitro- derivative, and from both the urethane and methylene compounds a mixture of the 4-nitro- and 2-nitro-derivatives is obtained.

Nitration of 2-acetylaminoanthraquinone yields 1-nitro-2-acetylaminoanthraquinone, whereas the urethane derivative gives a mixture of this together with 2-acetylamino-3-nitroanthraquinone. By hydrolysis the corresponding nitroaminoanthraquinones are obtained.

1:5- and 1:8-diaminoanthraquinone behave just as α-aminoanthraquinone, that is, the reaction is duplicated in the second ring.

Other methods for the preparation of nitroaminoanthraquinones are by the partial reduction of dinitroanthraquinones or from the chloronitroanthraquinones by Ullmann's reaction (*see* p. 395).

Nitration of Chloroanthraquinones.—The chloroanthraquinones nitrate with ease in sulphuric acid solution giving derivatives in which the nitro group is in the same nucleus with and *para* to the chlorine substituent. Thus α-chloroanthraquinone yields 1:4-chloronitroanthraquinone, m.p. 259°; 1:5-dichloroanthraquinone yields 1:5-dichloro-4:8-dinitroanthraquinone; while from 1:8-dichloroanthraquinone both 1:8-dichloro-4-nitro- and 1:8-dichloro-4:5-dinitroanthraquinone may be obtained.

Isomeric heteronuclear chloronitroanthraquinones can be prepared from the nitrosulphonates by treatment in aqueous solution with nascent chlorine, when quantitative replacement of the sulphonic group by this element takes place. They may also be obtained from chloroaminoanthraquinones by direct oxidation with ammonium persulphate.

Nitration of Hydroxyanthraquinones.—Nitrohydroxyanthraquinones are readily obtained by the direct nitration of hydroxyanthraquinones in sulphuric acid solution. Frequently the reaction is carried out in the presence of boric or arsenic acids in which case it is the boric or arsenic *ester* which is nitrated. The ester grouping not only protects the hydroxyanthraquinone against oxidation but it exerts a powerful directive influence upon the position taken up by the entering nitro group.

Normally the nitrating agent first attacks the α-position which is *para* to an α-hydroxyl group or is adjacent to a β-hydroxyl group; on further action it attacks the β-position which is contiguous with the hydroxyl radicle. Thus erythroxyanthraquinone yields 1-hydroxy-4-nitro-anthraquinone and finally 1-hydroxy-2:4-dinitroanthraquinone, whereas 2-hydroxyanthraquinone is converted first into 1-nitro-2-hydroxyanthraquinone and subsequently into 1:3-dinitro-2-hydroxyanthraquinone. In the case of heteronuclear dihydroxyanthraquinones the reaction is duplicated in the second nucleus. Alizarin in the presence of boric acid yields 3-nitroalizarin (*Alizarin Orange*), while in the presence of arsenic acid 4-nitroalizarin is obtained (*Alizarin Brown*).

The following are the more important products of direct nitration:

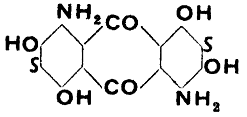
2-nitroquinizarin.
1-nitrohystazarin and 1:4-dinitrohystazarin.
4:8-dinitroanthrarufin and 2:4:6:8-tetranitroanthrarufin.
4:5-dinitrochrysazin and 2:4:5:7-tetranitrochrysazin.
1:5-dinitroanthraflavin.
1:3:6:8-tetranitroisoanthraflavin (first product).
3-nitropurpurin.
4-nitroanthragallol.

Flavopurpurin and anthrapurpurin, being alizarin derivatives, behave exactly as does alizarin; the 3-nitro derivative is formed in presence of boric acid, whereas the 4-nitro derivative is obtained when nitration is effected in presence of arsenic acid. Anthrachryson yields 2:4:6:8-tetranitroanthrachryson as first product.

The following dinitrodihydroxyanthraquinone disulphonates are obtained by nitration of the dihydroxyanthraquinone disulphonates and are of considerable industrial importance since on reduction the valuable series of *Alizarin Saphirol* acid dyestuffs is obtained. This range of colours is remarkable for its brightness combined with its great fastness to light (*v. infra*).

Anthrarufin-2:6-disulphonate
→ 4:8-dinitroanthrarufin-2:6-disulphonate.
Chrysazin-2:7-disulphonate
→ 4:5-dinitrochrysazin-2:7-disulphonate.
Anthraflavin-3:7-disulphonate
→ 1:5-dinitroanthraflavin-3:7-disulphonate.
*iso*Anthraflavin-3:6-disulphonate
→ 1:8-dinitro*iso*anthraflavin-3:6-disulphonate.
1:7-Dihydroxyanthraquinone-2:6-disulphonate → 4:8-dinitro-1:7-dihydroxyanthraquinone-2:6-disulphonate.

Anthrachryson-2:6-disulphonate yields 4:8-dinitroanthrachryson-2:6-disulphonate, which on reduction is converted into *Acid Alizarin Blue GR*.



Acid Alizarin Blue GR.

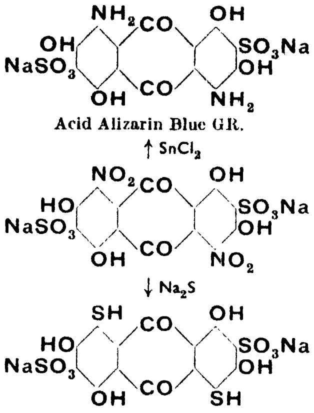
$[S=\cdot SO_3Na]$

The presence of a nitro group—a powerful auxochrome—greatly intensifies the tinctorial properties of the hydroxyanthraquinones. Both 3- and 4-nitroalizarins are used as dyestuffs and 3-nitroflavopurpurin appears in commerce as *Alizarin Orange G*. These dyestuffs moreover are polygenetic, that is, by using different lakes or mordants many different colours can be obtained with the same compound. 3-nitro-1:2:4:5:7:8-hexahydroxyanthraquinone (*Alizarin Cyanine Black G*), obtained by the hydroxylation of 3-nitroanthrapurpurin, yields a fine jet black when mordanted upon a chrome base.

Reduction of the Nitroanthraquinones.

The reduction of nitroanthraquinones can be effected by means of stannous chloride, sodium stannite, sodium amalgam, sodium sulphite, sulphur sesquioxide (a solution of sulphur in oleum) or sodium sulphide. Sodium sulphide is the most useful of these reagents both in the laboratory and industry and the reduction is carried out by stirring the nitroanthraquinone into a thin paste with aqueous sodium sulphide and then heating the mixture for a short time at 100°. At first the mass assumes a deep green colour due to formation of the intermediate hydroxylamino-compound but this changes with the application of heat to the colour, usually reddish-violet, of the aminoanthraquinone ; α-nitro- and 1:5- and 1:8-dinitroanthraquinones are converted by this treatment into 1-aminoanthraquinone, m.p. 245°, and 1:5- and 1:8-diaminoanthraquinones, m.p. 319° and 262° respectively, the yields being almost theoretical. 3- and 4-nitroalizarins give 3-amino alizarin (*Alizarin Maroon*) and 4-aminoalizarin (*Alizarin Cardinal*) and the four heteronuclear nitroanthraquinone sulphonates yield the corresponding aminoanthraquinone sulphonates.

In certain rare cases, however, simple reduction does not take place with this reagent, since *mercaptans* are sometimes produced by replacement of the nitro group, and in such cases reduction to the amino compound must be carried out by means of stannous chloride and hydrochloric acid. For example, 4:8-dinitroanthrachryson-2:6-disulphonate with stannous chloride yields 4:8-diaminoanthrachryson-2:6-disulphonate (*Acid Alizarin Blue GR*), whereas with sodium sulphide 4:8-dimercaptoanthrachryson-2:6-disulphonate (*Acid Alizarin Green B*) is produced (*see* top of next column for formulæ). Similarly 1:5-dihydroxy-4:8-dinitroanthraquinone-2:6-disulphonate ("dinitroanthrarufin disulphonate") with aqueous sodium sulphide at 75° yields 1:5-dihydroxy-4:8-dimercaptoanthraquinone-2:6-disulphonate (*Alizarin Emeraldol G*).

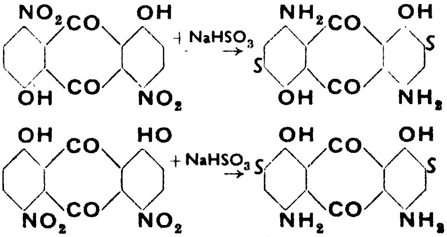


Acid Alizarin Blue GR.

Acid Alizarin Green B.

The important Alizarin Saphirol series of acid wool dyestuffs is obtained by the reduction of the corresponding dinitrodihydroxyanthraquinone disulphonates with stannous chloride.

Sodium hydrogen sulphite is a useful reagent for the reduction of nitroanthraquinones since it can frequently effect reduction together with simultaneous sulphonation of the nucleus. This seems to be particularly the case when hydroxyl groups are present and is well illustrated by the preparation of diaminoanthrarufin disulphonate and diaminochrysazin disulphonate (*Alizarin Saphirols*) by boiling dinitroanthrarufin and dinitrochrysazin respectively with aqueous sodium hydrogen sulphite.

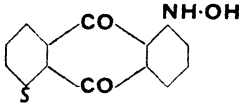


$[S=SO_3Na.]$

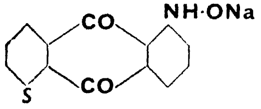
Partial reduction of dinitroanthraquinones can be accomplished by heating with *secondary* arylamines ; 1:5- and 1:8-dinitroanthraquinones by this treatment yield 1:5- and 1:8-nitroaminoanthraquinones respectively.

Intermediate Reduction Products.—By the reduction of 1-nitroanthraquinone and 1:5- and 1:8-dinitroanthraquinones with sodium stannite or glucose the intermediate hydroxylamino-compounds may be prepared in good yield. The hydroxylaminoanthraquinones are fairly stable red substances which dissolve in cold alkali with production of an intense deep green colour due to the formation of the soluble sodio-derivative.

Water-soluble nitroanthraquinones, such as the nitro-sulphonates, can be converted in good yield into the corresponding hydroxylamino-derivative by the action of aqueous sodium sulphide at 0°. The heteronuclear hydroxylaminoanthraquinone sulphonates thus formed are easily soluble in water giving crimson solutions which turn deep green on the addition of alkali owing to the formation of the sodio-derivative of the sodium salt.



Red.



Green.

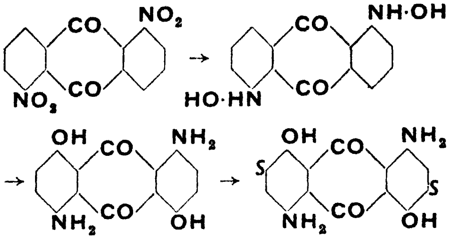
[$S = SO_3Na$]

Sodium 1-hydroxylaminoanthraquinone-5-, -6-, -7-, and -8-sulphonates may be used as indicators, changing colour at p_H values in the vicinity of $p_H = 11$, but they are of little colour permanence.

By limiting the amount of sodium sulphide and the duration of the reaction, and by maintaining the temperature below zero the nitro-sulphonates can be converted into the azoxy-sulphonates. These are sparingly soluble light brick-red compounds which are quantitatively reduced to the hydroxylamino-sulphonates by the further action of sodium sulphide at 0°, and to the amino-sulphonates by the action of the hot reagent.

The *a*-hydroxylaminoanthraquinones are of industrial importance owing to the fact that when they are heated to 100° in sulphuric acid solution the **N**-hydroxyl migrates to the nucleus, in the *para*-position to the nitrogen, giving good yields of the *para*-*aa*-aminohydroxyanthraquinones. By this means 1:4-aminohydroxyanthraquinone, m.p. 215°, is obtained from *a*-nitroanthraquinone while 1:5-diamino-4:8-dihydroxy- and 1:8-diamino-4:5-dihydroxyanthraquinones are obtained from 1:5- and 1:8-dinitroanthraquinones respectively. Similarly the four heteronuclear hydroxylaminoanthraquinone sulphonates yield 1-amino-4-hydroxyanthraquinone -5-, -6-, -7-, and -8-sulphonates which are all dark microcrystalline compounds giving intense violet aqueous solutions. Their *sulphates* are difficultly soluble, mustard-coloured amorphous powders which are precipitated when strong sulphuric acid is added to their concentrated aqueous solutions; they serve as useful substances by which purification of the parent compound may be effected.

An interesting illustration of the above series of reactions is the direct formation of Alizarin Saphirol from 1:5-dinitroanthraquinone by treatment with a solution of sulphur in oleum (sulphur sesquioxide). First, reduction to 1:5-dihydroxylaminoanthraquinone takes place, followed by migration of the **N**-hydroxyl to the nucleus, accompanied by simultaneous reduction and sulphonation as the temperature is raised.



Alizarin Saphirol.

The Aminoanthraquinones.

The simple primary aminoanthraquinones are all coloured substances which, however, possess very limited tinctorial properties although some of the aminohydroxyanthraquinones together with their sulphonates (*e.g.* *Alizarin Maroon* and *Alizarin Saphirol*, etc.) are valuable dyestuffs.

The arylaminoanthraquinones, on the other hand, and the acylaminoanthraquinones in which the acyl group is derived from a dibasic aliphatic or a monobasic or dibasic aromatic acid are powerful vat dyestuffs. In addition, the arylaminoanthraquinone sulphonates form a group of important soluble acid wool dyes.

The aminoanthraquinones themselves exhibit less pronounced basic properties than the aminobenzenes and the aminonaphthalenes but they undergo, with modifications, most of the reactions of aromatic amino compounds. Diazotisation is effected by treating a dilute hydrochloric or sulphuric acid suspension of the aminoanthraquinone with sodium nitrite, but it is better to add the finely powdered nitrite to the *solution* of the aminoanthraquinone in cold concentrated sulphuric acid; on pouring the solution into brine the diazonium sulphate is precipitated in the microcrystalline form. The diazonium salts, particularly the sulphates, are remarkably stable substances which can in most cases be boiled with water without any decomposition. Many of them, moreover, are difficultly soluble in water. Replacement of the diazonium group by hydroxyl is effected by heating the diazonium sulphate with dilute sulphuric acid at temperatures ranging from 120° to 180°. Replacement of the amino group by chlorine is accomplished by diazotising in concentrated sulphuric acid and then adding a solution of cuprous chloride in concentrated hydrochloric acid. After standing for some time at a temperature of about 60° the corresponding chloroanthraquinone is precipitated by the addition of water. Good yields of the *a*-cyano-derivatives can be obtained by heating the *a*-diazonium sulphate with aqueous cuprous cyanide at 100°; with *β*-diazonium groups the yields are very poor.

When *β*-aminoanthraquinone is boiled with antimony pentachloride in nitrobenzene solution flavanthrene (*Indanthrene Yellow G*) is obtained in 30% yield. Fusion of *β*-aminoanthraquinone with potassium hydroxide yields *Indanthrene Blue R*, which was the first of the anthraquinonoid vat dyes to be placed on the market (*v. infra*).

The aminoanthraquinones may be prepared in good yield by the reduction of the nitroanthraquinones but far more important is their formation by the replacement of halogen, sulphonic, hydroxyl, and nitro radicles by the amino group. This is effected by heating the sulphonate or the halogen-, nitro-, or hydroxylanthraquinone under pressure at fairly high temperatures with aqueous ammonia. Halogenanthraquinones react readily in the presence of copper salts at 200° to give excellent yields of the aminoanthraquinones. This is one of the methods by which 1- and 2-aminoanthraquinones and 1:5-, 1:8-, 2:6-, and 2:7-diaminoanthraquinones are manufactured on the industrial scale. Halogen substituents in *a*-positions are more reactive than *β*-halogens and, moreover, the presence of substituents, even in the non-halogenated nucleus, frequently enhances the reactivity of the halogen towards replacement. Thus sodium 1-chloroanthraquinone -5-, -6-, -7-, and -8-sulphonates react with ammonia at 100° in the presence of traces of copper sulphate to give almost quantitative yields of the corresponding aminoanthraquinone sulphonates. Sodium 2-chloroanthraquinone -6- and -7-sulphonates do not react at all at 100°, but both sodium 2-chloroanthraquinone -3:6- and -3:7-disulphonates react smoothly at this temperature to give excellent yields of sodium 2-aminoanthraquinone-3:6- and -3:7-disulphonates. Sodium 1-aminoanthraquinone -2:5-, -4:5-, -2:6-, -4:6-, and -2:7-disulphonates are similarly prepared from the corresponding chloroanthraquinone disulphonates; they are all dark micro-crystalline powders which are very soluble in water with the production of an intense red colour. With 4:8-dibromanthrarufin-2:6-disulphonate the reaction takes place at 40°, giving good yields of Alizarin Saphirol.

The replacement of the sulphonic radicle by the amino group also takes place with great facility. The usual procedure is to heat the sodium sulphonate with 10–25% aqueous ammonia to 180° for several hours in the presence of a small amount of barium chloride or of an oxidising agent such as manganese dioxide or arsenic acid.

$$\mathrm{C_{14}H_7O_2{\cdot}SO_3Na + NH_3 \rightarrow C_{14}H_7O_2{\cdot}NH_2 + NaHSO_3}$$

The sulphite which is formed during the reaction tends to attack the nucleus at the high temperatures employed unless it is oxidised to the harmless sulphate or removed from the sphere of the reaction as insoluble barium sulphite. Both 1- and 2-amino- and 1:5-, 1:8-, 2:6-, and 2:7-diamino-anthraquinones can be prepared in good yields by this method.

Nitro- and hydroxyanthraquinones react with ammonia with difficulty giving poor yields even at elevated temperatures. Alizarin and chrysazin, for example, give small quantities of 1:2- and 1:8-hydroxyaminoanthraquinones; it is noteworthy that in the case of alizarin it is the *β*-hydroxyl which is replaced.

An important reaction for the preparation of an aminoanthraquinone from a chloroanthraquinone without the use of an autoclave is Ullmann's sulphonamide process. The chloroanthraquinone is boiled in an inert solvent such as nitrobenzene with *p*-toluene sulphonamide in the presence of a copper salt and an alkali carbonate. The resulting *p*-toluene sulphonamidoanthraquinone is easily hydrolysed by heating with dilute mineral acids to give the aminoanthraquinone:

$$\mathrm{C_{14}H_7O_2Cl + NH_2{\cdot}O_2S{\cdot}C_6H_4Me \rightarrow C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_{14}H_7O_2 + HCl}$$

$$\mathrm{C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_{14}H_7O_2 + H_2O \rightarrow C_{14}H_7O_2{\cdot}NH_2 + HO_3S{\cdot}C_6H_4Me}$$

If the N-substituted toluene sulphonamide is used (obtained from toluene sulphonchloride and the desired amine) the N-substituted aminoanthraquinone is formed. The yields by Ullmann's process are nearly theoretical.

Amino groups can also be directly introduced into an *a*-position by the action of a solution of hydroxylamine and ferrous sulphate in concentrated sulphuric acid, but the yields are very poor.

The Alkyl- and Arylaminoanthraquinones.—The alkylaminoanthraquinones can be obtained by the alkylation of aminoanthraquinones by heating them with the requisite alkyl halide or sulphate at 100° or by heating the aminoanthraquinone together with sulphuric acid and an alcohol at 180°.

Condensation between aminoanthraquinones and aryl halides such as chlorobenzene, *p*-dichlorobenzene, *pp′*-dichlorodiphenyl, *pp′*-dichlorodiphenylmethane, and chloroanthraquinones takes place with ease at 200°, but only in the presence of a copper salt and an alkali carbonate to absorb the hydrogen chloride evolved.

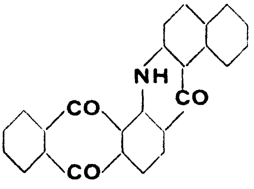
Far more important, however, is the preparation of the alkyl- and arylaminoanthraquinones by the direct introduction of the alkylamino and arylamino residues into the anthraquinone nucleus. This is effected by condensing halogen-, nitro-, and hydroxy-anthraquinones with primary and secondary aliphatic and primary aromatic amines; condensation does not usually take place with secondary arylamines. The usual procedure is to heat the chloro-, nitro-, or hydroxy-anthraquinone together with the amine in the presence of a small amount of a copper salt and an alkali carbonate either alone or in a high-boiling inert solvent such as nitrobenzene, naphthalene or amyl alcohol. The yields obtained by this method, especially with halogen-anthraquinones, are excellent. Halogen atoms in *a*-positions are more reactive than *β*-halogen substituents; for example, 2:4-dibromoerythroxyanthraquinone may be converted in good yield into 1-hydroxy-2-brom-4-*p*-toluidoanthraquinone by condensation with 1 molecule of *p*-toluidine.

Although *a*-nitroanthraquinones condense with great difficulty with ammonia they react readily with the above type of amine with production of very good yields of the arylamino-compound.

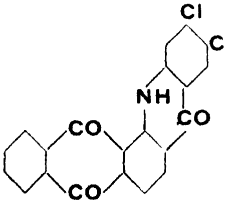
Condensation between amines and hydroxyanthraquinones takes place with some difficulty, but it usually proceeds quite smoothly in the presence of boric acid; in this case it is the *boric* ester of the hydroxylanthraquinone which reacts. The reactivity of the hydroxylanthraquinones is also greatly increased by reduction to the leuco-compound; the condensation, especially with arylamines, then usually takes place at temperatures as low as 100° and on mild oxidation of the product the corresponding arylaminoanthraquinone is obtained in good yield.

The arylaminoanthraquinones form a group of vat dyes but they are usually sulphonated in order to confer solubility and thereby convert them into substantive acid colours for the dyeing of wool and silk. On sulphonation the more easily sulphonated benzene nucleus is attacked and in the case of the *p*-toluidinoanthraquinones the sulphonic group enters the position *ortho* to the nitrogen-bearing carbon atom. Isomeric compounds possessing slightly different colour hues are obtained by condensing the halogen-, nitro-, or hydroxy-anthraquinones with *p*-toluidinesulphonic acid $[CH_3:HSO_3:NH_2=1:2:4]$. When the sulphonation of arylaminoanthraquinones is carried out *in the presence of boric acid*, however, different products are obtained in which the sulphonic group is in the anthraquinone nucleus.

Acridones and Thioxanthones derived from Anthraquinone.—Condensation of an *ortho*-chloroanthraquinone carboxylic acid with an arylamine or, conversely, condensation of a chloroanthraquinone with an *ortho*-aminocarboxylic acid by the above method yields products which are readily converted, by treatment with sulphuric acid, into anthraquinone acridones and these are powerful vat dyestuffs. Thus 1-chloroanthraquinone-2-carboxylic acid condenses with β-naphthylamine and yields, after closure of the acridone ring, *Indanthrene Red BN*. Similarly α-chloroanthraquinone and anthranilic acid give a product which on closure of the acridone ring and chlorination with sulphuryl chloride is converted into *Indanthrene Red-Violet 2RN*.



Indanthrene Red BN.



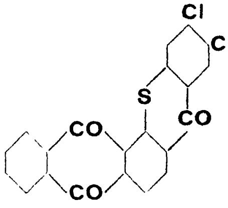
Indanthrene Red-Violet 2RN.

In the same manner 1:5-dichloroanthraquinone and anthranilic acid yield *Indanthrene Violet RN*; in this case the reaction is duplicated in the other ring.

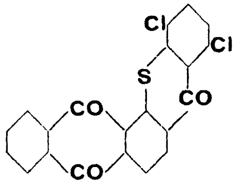
Similarly 1-cyano-2-halogenoanthraquinone condenses with arylamines and also α-aminoanthraquinone condenses with *ortho*-bromonitriles to form cyanoarylaminoanthraquinones which readily undergo ring closure to the corresponding anthraquinone-acridone on treatment for a short time with sulphuric acid.

The phenylaminoanthraquinone carboxylic acids are intensely coloured but have little or no affinity for vegetable fibres. With the formation of the acridone ring, however, powerful dyeing properties appear, and these, it seems, are not so much dependent upon the presence of the acridone ring *per se* as it is upon the reciprocal action of the -NH- and -CO- groupings which have become drawn into close proximity with one another. This assumption is well supported by the well-known fact that whereas the aminoanthraquinones are of little use as colouring matters the benzoyl- and acyl-aminoanthraquinones are strong vat dyestuffs.

In the same manner 1-chloroanthraquinone-2-carboxylic acid condenses readily with 3:4-dichlorothiophenol in aqueous alkaline solution to yield a compound which on closure of the thioxanthone ring is converted into *Indanthrene Golden Orange GN*. Similarly with 2:5-dichlorothiophenol *Indanthrene Yellow GN* is obtained.

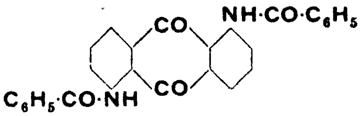


Indanthrene Golden Orange GN.



Indanthrene Yellow GN.

The Acyl- and Aroylaminoanthraquinones.—The aminoanthraquinones can be acylated and aroylated with ease by heating them with acid chlorides, *e.g.* phosgene, acetyl, succinyl, and benzoyl chlorides, or by heating them with the acid anhydride or the acid itself, *e.g.* benzoic acid, salicylic acid, etc., at fairly high temperatures. They constitute a group of valuable vat dyestuffs of especial importance to the calico printer, *e.g.* *Caledon Yellow 3G*.



Caledon Yellow 3G.

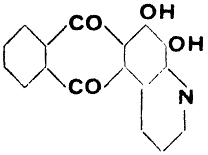
Anthraquino-quinolines. — Aminoanthraquinones undergo the Skraup reaction when heated with glycerol and sulphuric acid together with a mild oxidising agent. The hydroxy-anthraquino-quinolines are important vat dyestuffs, the better known of which are :

Alizarin Blue RR obtained from 3-amino-alizarin.

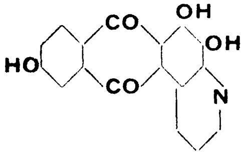
Alizarin Black P obtained from 3-amino-flavopurpurin.

Alizarin Green obtained from 4-amino-alizarin.

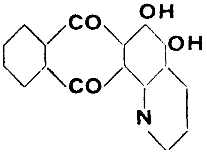
Alizarin Blue S and Alizarin Black S are the bisulphite compounds of the first two dyestuffs respectively.



Alizarin Blue RR



Alizarin Black P



Alizarin Green.

Halogenation of Aminoanthraquinones.—Aminoanthraquinones are readily halogenated when treated in organic solvents with bromine, chlorine or sulphuryl chloride or when treated in aqueous suspension with nascent chlorine. Bromination of α-aminoanthraquinone gives 1-amino-2-bromoanthraquinone, m.p. 182°, and, on further treatment, 1-amino-2:4-dibromoanthraquinone, m.p. 226°. Similarly 1:5-diaminoanthraquinone yields 1:5-diamino-2:4:6:8-tetrabromoanthraquinone, m.p. above 300° ; further bromination yields the hexabromo-derivative.

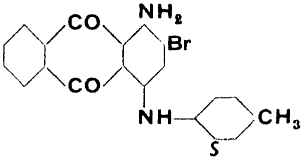
Bromination of β-aminoanthraquinone yields first 2-amino-3-bromoanthraquinone, m.p. 311°, and finally 2-amino-1:3-dibromoanthraquinone, m.p. 241°. Similarly 2:6-diaminoanthraquinone gives 2:6-diamino-1:3:5:7-tetrabromoanthraquinone.

Chlorination of α-aminoanthraquinone itself gives rise to a complex mixture of N-chloro compounds from which nothing definite can be isolated. Chlorination of α-acetylaminoanthraquinone, however, yields 1-acetylamino-4-chloroanthraquinone from which 1-amino-4-chloroanthraquinone, m.p. 180°, is obtained by hydrolysis.

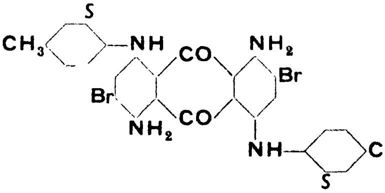
Chlorination of β-aminoanthraquinone gives 1:3-dichloro-2-aminoanthraquinone, m.p. 231°, as first product, whereas when β-acetylaminoanthraquinone is treated with chlorine 1-chloro-2-acetylaminoanthraquinone is produced in good yield ; hydrolysis of the latter yields 1-chloro-2-aminoanthraquinone, m.p. 237°.

The above reactions may be summarised by the following rules. With α-aminoanthraquinone the first halogen enters the *ortho* position to the amino group and the second halogen the *para* position ; in the case of α-acetylaminoanthraquinone this order is inverted. With β-aminoanthraquinone the first halogen enters the β-position contiguous to the amino group and the second halogen enters the α-position adjacent to the amino group ; in the case of β-acetylaminoanthraquinone this order is again inverted.

The α-bromine substituent in both 1:3-dibromo-2-aminoanthraquinone and 1-amino-2:4-dibromoanthraquinone is exceedingly labile and in presence of almost any aromatic amine this α-bromine atom is removed with formation of 2-amino-3-bromo- and 1-amino-2-bromoanthraquinone respectively. With sulphuric acid 1-amino-2:4-dibromoanthraquinone is rapidly converted into 1-amino-2-bromo-4-hydroxyanthraquinone, while with *p*-toluidine at low temperatures it reacts to give 1-amino-2-bromo-4-*p*-toluidoanthraquinone ; sulphonation of the latter yields *Alizarin Pure Blue B.* Similarly 1:5-diamino-2:4:6:8-tetrabromoanthraquinone condenses at low temperatures with *p*-toluidine to give a product which on sulphonation is converted into *Anthraquinone Blue SR.*



Alizarin Pure Blue B.



Anthraquinone Blue SR.

The Hydroxyanthraquinones.

The two monohydroxy- and the ten theoretically possible dihydroxy-anthraquinones are all known, but of the fourteen possible trihydroxyanthraquinones only nine are known at the present time. They are usually referred to by special names and most of them are of considerable commercial importance (*see* Alizarin and Allied Dyestuffs).

The Chloroanthraquinones.

The standard method for the preparation of the chloroanthraquinones is by the direct replacement of sulphonic groups by chlorine. This is carried out by slowly adding aqueous potassium or sodium chlorate to a boiling aqueous-hydrochloric acid solution of the sodium anthraquinone mono- or disulphonate. The nascent chlorine thus generated reacts quickly with the sulphonate the product being thrown down as a flocculent precipitate. If the sulphonate used is pure, *i.e.* free from isomeric sulphonates, the precipitated chloroanthraquinones are usually crystalline and sharp-melting, the crystals frequently attaining large dimensions. Similarly by using potassium bromate and hydrobromic acid the corresponding bromoanthraquinones are obtained.

The Mono- and Dichloroanthraquinones.—By the above methods both α- and β-monochloro- and 1:5-, 1:6-, 1:7-, and 1:8-dichloro-anthraquinones are readily prepared. In the case of sodium anthraquinone-1:6-disulphonate the intermediate sodium 1-chloroanthraquinone-6-sulphonate is formed as an insoluble flocculent precipitate in good yield. When this salt is suspended in a large volume of water and again treated with nascent chlorine in like manner, it is gradually converted into 1:6-dichloroanthraquinone.

Similar treatment of sodium anthraquinone-2:6- and -2:7-disulphonates, however, only effects replacement of *one* sulphonic group giving an insoluble precipitate of sodium 2-chloroanthraquinone-6- and -7-sulphonates respectively. The second sulphonic group completely resists replacement by this method.

Both 2:6- and 2:7-dichloroanthraquinones are prepared by heating the corresponding disulphonyl chlorides or chloro-sulphonyl chlorides with thionyl chloride under pressure; sulphur dioxide is eliminated with formation of the dichloroanthraquinone. They may also be obtained from 2:6- and 2:7-diaminoanthraquinones by diazotising in concentrated sulphuric acid and treatment with cuprous chloride or by the action of nascent chlorine on sodium *meso*-dichloroanthracene-2:6- and -2:7-disulphonates.

The homonuclear dichloroanthraquinones are prepared from amino- and hydroxyanthraquinones or by nuclear synthesis (*v. infra*). Replacement of the amino group by chlorine in 1-chloro-2-amino- and 1-chloro-4-amino-anthraquinone yields 1:2- and 1:4-dichloroanthraquinones respectively, while 1:3-dichloroanthraquinone is produced by the deamination of 1:3-dichloro-2-aminoanthraquinone. 1:4-dichloroanthraquinone may also be obtained by the chlorination of erythroxyanthraquinone with sulphuryl chloride and subsequent replacement of the hydroxyl group in the 1:4-chlorohydroxyanthraquinone thus formed by treatment with phosphorus pentachloride.

The melting points of the mono- and dichloroanthraquinones are:—

Position of substituents.	M.p.
1	162°
2	208°
1:2	203°
1:3	208°
1:4	186°–187°
1:5	244°–245°
1:6	203°
1:7	213°–214°
1:8	201°
2:3	261°
2:6	280°–282°
2:7	209°–210°

The Trichloroanthraquinones (11 known).—The trichloroanthraquinones are obtained principally by monosulphonating a dichloroanthraquinone or, alternatively, by disulphonating a monochloroanthraquinone, separating the various isomeric products in each case and then individually replacing the sulphonic group or groups by chlorine by treatment with nascent chlorine as described above. Replacement takes place with production of good yields, except in the case of 2:3-dichloroanthraquinone-6-sulphonate, which completely resists attack by nascent chlorine. With 2-chloroanthraquinone-3:6- and -3:7-disulphonates the final product of chlorination is 2:3-dichloroanthraquinone-6-sulphonate.

The homonuclear trichloroanthraquinones are obtained by special methods. The 1:2:3-compound is prepared by replacement of the amino group in 1:3-dichloro-2-aminoanthraquinone by chlorine and the 1:2:4-isomeride is obtained from 1-hydroxy-2:4-dichloroanthraquinone (*v.i.*) by treatment with phosphorus pentachloride.

The melting points of the trichloroanthraquinones are:—

Position of substituents.	M.p.
1:2:3	194°–195°
1:2:4	186°
1:2:5	235°–236°
1:2:6	222°–223°
1:2:7	225°–226°
1:3:6	212°–213°
1:3:7	216°–217°
1:4:5	258°
1:4:6	236°
2:3:5	227°–228°
2:3:6	245°

1:4:5:8-tetrachloroanthraquinone, m.p. 342°, is obtained by the chlorination of both 1:8-dichloroanthraquinone-4:5-disulphonate and 1:5-dichloroanthraquinone-4:8-disulphonate and also by the direct chlorination of anthraquinone itself in oleum solution. 1:2:3:4-tetrachloroanthraquinone, m.p. 191°, is produced by the condensation of tetrachlorophthalic anhydride with benzene. Other tetrachloroanthraquinones of uncertain constitution are obtainable from various dichloroanthraquinone disulphonates.

Hydroxyanthraquinones are chlorinated and brominated with ease when treated with the nascent halogen at temperatures above 100° in dilute sulphuric or acetic acid suspension. A much used method of chlorination is to boil a nitrobenzene solution of the hydroxyanthraquinone with sulphuryl chloride. Less important is chlorination by means of aqueous alkaline sodium hypochlorite. The following are prepared by direct chlorination of the parent hydroxyanthraquinone:

1-*hydroxy*-4-*chloro*- and 1-*hydroxy*-2:4-*dichloroanthraquinone*; 1-*chloro*-2-*hydroxyanthraquinone*; 4-*chloro*- and 4:8-*dichloroanthrarufin*; 4:5-*dichlorochrysazin*; 2-*chloroquinizarin*; 3-*chloroalizarin*.

Similarly, the corresponding series of bromine derivatives are obtained by bromination of the hydroxyanthraquinones.

Anthraflavin, *iso*anthraflavin, anthrapurpurin, and flavopurpurin also yield chloro derivatives the constitutions of which have not as yet been determined. Anthragallol and purpurin are brominated in the 4- and 3-positions respectively.

In many cases the sulphonic groups in hydroxyanthraquinone sulphonates can be replaced by chlorine or bromine by treatment of the parent compound in aqueous solution with the nascent halogen as described above. Frequently, however, if excess of the halogen is employed it further attacks the nucleus in the α-positions with production of more highly chlorinated or brominated hydroxyanthraquinones. The following are the more important preparations effected by this method:

Erythroxy-2-sulphonate → *1-hydroxy-2-bromoanthraquinone* and *1-hydroxy-2:4-dibromoanthraquinone.*

Anthrarufin-2:6-disulphonate → *2:6-dibromoanthrarufin.*

Alizarin-3-sulphonate → *3-chloroalizarin.*

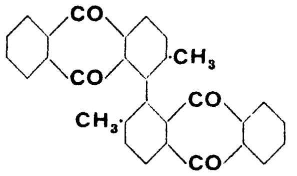
Chrysazin-2:7-disulphonate → *2:4:5:7-tetrabromochrysazin.*

Anthrachryson-2:6-disulphonate → *2:6-dibromoanthrachryson* and *2:4:6:8-tetrabromoanthrachryson.*

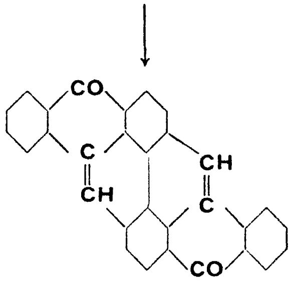
When anthrarufin-2:6-disulphonate and chrysazin-2:7-disulphonate are treated with bromine in aqueous solution at 140° the sulphonic group is *not* replaced, but bromination of the nucleus in the α-positions *para* to the hydroxyl takes place, with production of *4:8-dibromoanthrarufin-2:6-disulphonate* and *4:5-dibromochrysazin-2:7-disulphonate* respectively. The α-bromine substituents in these compounds are very reactive and are readily replaced by amino groups with formation of Alizarin Saphirols on treatment with aqueous ammonia.

The **chloroanthraquinones** are light lemon yellow crystalline substances which are the more deeply coloured the more α-chlorine substituents they contain; 2:3:6-trichloroanthraquinone is almost colourless. They are of considerable industrial importance owing to the fact that the chlorine substituents, especially those in α-positions, can with ease be replaced by a variety of groups such as amino, alkylamino, arylamino, and hydroxyl by methods which have been described above.

By heating α-chloroanthraquinones in nitrobenzene solution with potassium acetate and a *trace* of copper powder the chlorine is removed and replaced by hydrogen. Thus 1-chloroanthraquinone and 1-chloro-4-methylanthraquinone yield anthraquinone and α-methylanthraquinone respectively. When the reaction is carried out in the absence of potassium acetate and in the presence of an *excess* of copper powder the chlorine substituent is removed and then two anthraquinonyl residues link up with formation of 1:1′-dianthraquinonyl. In this manner 1-chloro-2-methylanthraquinone condenses with itself to give 2:2′-dimethyl-1:1′-dianthraquinonyl; treatment of this compound with alcoholic potash causes aldol condensation to take place between each methyl group and the nearest carbonyl in the *other* nucleus, with the subsequent elimination of two molecules of water and formation of *Pyranthrone.*

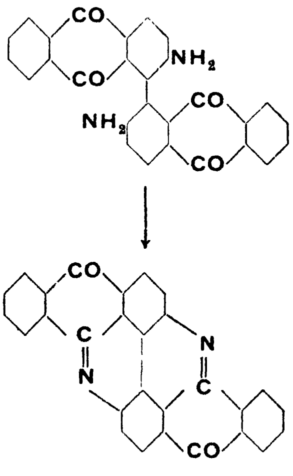


2:2′-Dimethyl 1:1′-dianthraquinonyl.



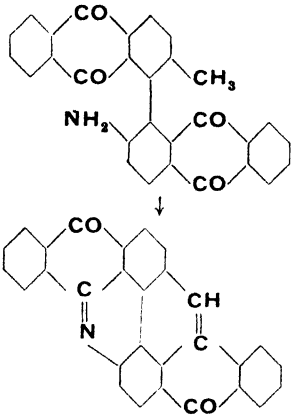
Pyranthrone.

In exactly the same way 1-chloro-2-aminoanthraquinone condenses with itself to form 2:2′-diamino-1:1′-dianthraquinonyl, which on ring closure yields *Flavanthrene* (Indanthrene Yellow G).



Flavanthrene.

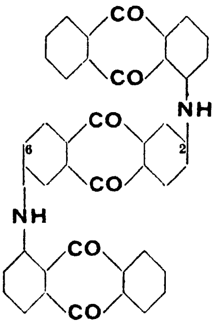
Similarly, by the condensation of 1-chloro-2-methylanthraquinone with 1-chloro-2-aminoanthraquinone and subsequent ring closure *Pyranthridone* is formed.



Pyranthridone.

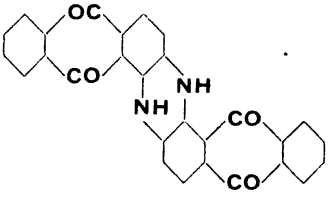
By using substituted 1-chloro-2-methyl- and 1-chloro-2-amino-anthraquinones a great variety of substituted flavanthrenes, pyranthrones and pyranthridones can easily be obtained. These compounds constitute a group of valuable vat dyestuffs possessing an extraordinary fastness to light.

Chloroanthraquinones condense with aminoanthraquinones when heated together in nitrobenzene or naphthalene solution, in the presence of an alkali carbonate and copper powder, with the elimination of hydrogen chloride and formation of anthrimides, dianthrimides and trianthrimides which are powerful vat dyestuffs, *e.g. Indanthrene Red R.*

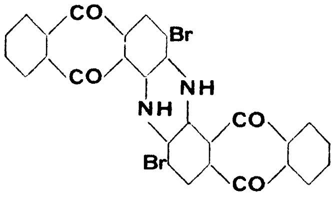


Indanthrene Red R (2 : 6-dichloroanthraquinone and 1-aminoanthraquinone).

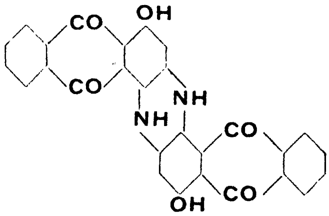
In the same way *ortho*-bromoaminoanthraquinones condense with themselves, but in this case compounds containing the *hydroazine nucleus* or *true indanthrenes* are produced. Thus 1-amino-2-bromo-4-hydroxyanthraquinone condenses with itself to give Indanthrene Blue 5G and two molecules of 1 : 3-dibromo-2-aminoanthraquinone condense to yield Indanthrene Blue 3GT [Caledon Blue GC]. Indanthrene itself is obtained by fusion of β-aminoanthraquinone with potash and is the parent compound of this important group of vat dyestuffs.



Indanthrene (Indanthrene Blue R).



Indanthrene Blue 3GT



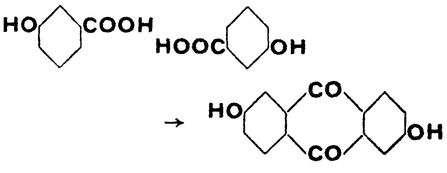
Indanthrene Blue 5G.

Halogen substituents in α-positions can be removed by treatment with zinc dust and ammonia ; for example, 1 : 2 : 3 : 4-tetrachloroanthraquinone yields 2 : 3-dichloroanthraquinone with this reagent.

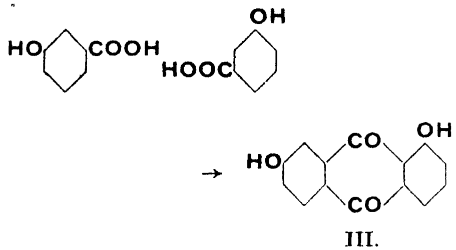
NUCLEAR SYNTHESES OF ANTHRAQUINONE AND ITS DERIVATIVES.

There are several methods by which anthraquinone derivatives may be prepared from compounds of the benzene series. These are known as "nuclear syntheses" and are termed "Kernsynthesen" in the German literature.

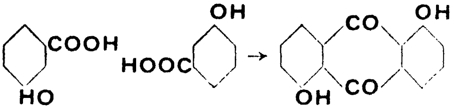
1. The Rufi-condensation.—Two molecules of a substituted benzoic acid are condensed by means of a dehydrating agent such as sulphuric acid. The first known example of this condensation was with *m*-hydroxybenzoic acid, which yields anthraflavin (I) together with smaller amounts of anthrarufin (II) and metabenzdioxyanthraquinone (III).



I.

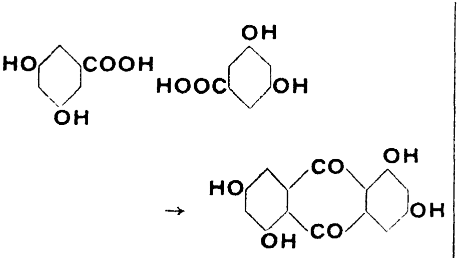


III.

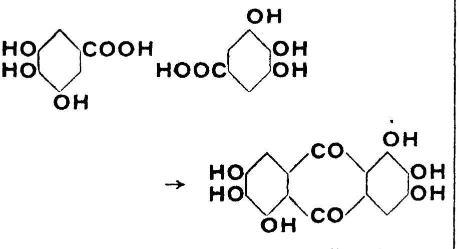


II.

The only rufi-condensations which are of industrial value are those in which only *one* product can result whichever way round the molecules condense. These are the preparation of anthrachryson and rufigallic acid from 2 : 5-dihydroxybenzoic acid and gallic acid respectively.



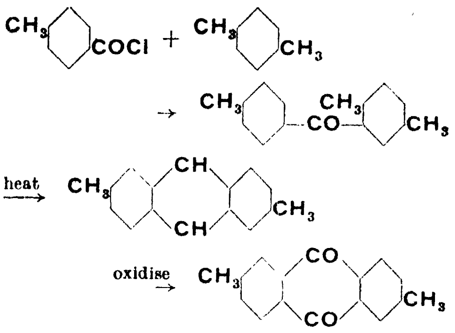
Anthrachryson.



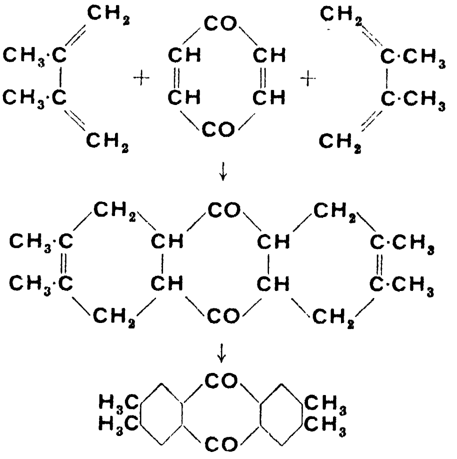
Rufigallic acid.

A modification of this method is the condensation of two molecules of a substituted benzoyl chloride by means of aluminium chloride ; for example, *m*-toluyl chloride yields 2 : 6-dimethylanthraquinone as chief product.

II. Pyrolysis of a Substituted Benzophenone.—An example of this method of synthesis is the condensation of *p*-toluyl chloride with *p*-xylene with the formation of trimethylbenzophenone ; pyrolysis of the latter yields 2 : 6-dimethylanthracene, which on mild oxidation is converted into 2 : 6-dimethylanthraquinone.

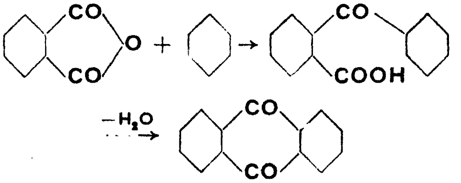


III. Condensation of Butadienes with *para*-Quinones (Euler and Diels synthesis).—Two molecules of ββ-dimethylbutadiene and one molecule of benzoquinone yield a compound which on oxidation is converted into 2 : 3 : 6 : 7-tetramethylanthraquinone.



Similarly condensation of β-chlorobutadiene (1 mol.) with naphthaquinone (1 mol.) yields β-chloroanthraquinone. The method has a limited application owing to the inaccessibility of the substituted butadienes.

IV. Synthesis from Phthalic Anhydride and Benzene.—This is by far the most important synthesis of anthraquinone and considerable quantities of anthraquinone itself and its derivative are manufactured by this method. Phthalic anhydride condenses with benzene in the presence of anhydrous aluminium chloride with the formation of benzoyl benzoic acid and on heating this with sulphuric acid ring closure takes place with the elimination of water and formation of anthraquinone.



On the industrial scale the benzoyl benzoic acid is frequently heated with 20–40% oleum at high temperatures, in which case ring closure takes place together with subsequent sulphonation. By the employment of substituted phthalic anhydrides and various derivatives of benzene a great variety of substituted anthraquinones may be obtained. The benzoyl benzoic acid method is of wide application and the yields are frequently nearly theoretical. Usually anhydrous aluminium chloride is used as condensing agent the reaction being carried out in excess of one of the reactants, *e.g.* benzene or toluene, but diluent materials such as carbon disulphide, petroleum ether and acetylene tetrachloride are also employed. Acetylene tetrachloride is the best diluent since it dissolves considerable quantities of aluminium chloride, thereby increasing the yields and, moreover, it almost completely inhibits the formation of *phthaleins* when phenols are undergoing condensation with phthalic anhydride. In the case of phenols, condensation is frequently effected by fusion with phthalic anhydride and anhydrous boric acid at 180° when the hydroxybenzoyl benzoic acid is produced in good yield without the formation of phthaleins.

The position taken up by the phthaloyl residue on entering the benzene nucleus is usually *ortho* or *para* to a substituent already in that nucleus. The condensation of phthalic anhydride with alkyl benzenes, monohalogen benzenes, phenols and their ethers takes place with great ease but with the dichlorobenzenes the yields are not so good. Dichlorophthalic anhydrides however, condense with benzene with production, after ring closure, of excellent yields of the homonuclear dichloroanthraquinones. Negative substituents in the benzene nucleus in all cases hinder the condensation; for example, phthalic anhydride will not condense with nitrobenzene although nitrophthalic anhydride condenses readily with benzene.

Ring closure to form the anthraquinone is usually carried out by heating for a short time on the water bath with sulphuric acid or oleum with or without the addition of boric acid. In some cases this treatment is ineffective, although the corresponding *benzyl benzoic* acid, obtained by reduction, will frequently react with ease, and on oxidation of the substituted anthrone thus produced, the desired anthraquinone derivative is obtained. In other cases more substituents must be introduced into the benzoylbenzoic acid nucleus before ring closure can be effected. For example, the dihydroxybenzoylbenzoic acid obtained from phthalic anhydride and resorcinol resists all attempts at ring closure; on bromination, however, a dibromodihydroxybenzoyl benzoic acid is formed which readily gives 1:3-dihydroxy-2:4-dibromoanthraquinone on treatment with sulphuric acid.

The following are the more important syntheses carried out by this method:

Phthalic anhydride and—
Benzene → anthraquinone.
Toluene → 2-methylanthraquinone.
o-Xylene → 1:2- and 2:3-dimethylanthraquinone.
m-Xylene → 1:3-dimethylanthraquinone.
p-Xylene → 1:4-dimethylanthraquinone.
Chlorobenzene → 2-chloroanthraquinone.
o-Dichlorobenzene → 2:3-dichloroanthraquinone.
m-Dichlorobenzene → 1:3-dichloroanthraquinone.
p-Dichlorobenzene → 1:4-dichloroanthraquinone.
p-Chlorotoluene → 1-chloro-4-methylanthraquinone.
p-Chlorophenol → 1-chloro-4-hydroxyanthraquinone.
Phenol → 1- and 2-hydroxyanthraquinone.
Catechol → alizarin and hystazarin.
Quinol → quinizarin.
Pyrogallol → anthragallol.
Hydroxyquinol → purpurin.

3:4-Dichlorophthalic anhydride and benzene → 1:2-dichloroanthraquinone.
4:5-Dichlorophthalic anhydride and benzene → 2:3-dichloroanthraquinone.
3:6-Dichlorophthalic anhydride and benzene → 1:4-dichloroanthraquinone.
3:6-Dichlorophthalic anhydride and chlorobenzene → 1:4:6-trichloroanthraquinone.
4:5-Dichlorophthalic anhydride and chlorobenzene → 2:3:6-trichloroanthraquinone.
Hemipinanhydride and benzene → alizarin.
Hemipinanhydride and quinol → quinalizarin.

References.—A comprehensive account of the chemistry of anthraquinone and allied ring systems together with full references and indexes to the original literature and patent specifications up to the year 1929 is given by Houben, "Das Anthracen und die Anthrachinone" (G. Thieme, Leipzig).

The actual patent specifications are given in full in Friedländer's "Fortschritte der Teerfarbenfabrikation."

The constitution of anthraquinonoid dyestuffs together with their preparation and mode of application is given in the "Colour Index" (Rowe).

For work after 1929 Amer. Chem. Abstr. should be consulted. The chloroanthraquinone mono- and disulphonates, aminoanthraquinone mono- and disulphonates, dichloroanthraquinones, trichloroanthraquinones, hydroxylaminoanthraquinone monosulphonates, and the aminohydroxyanthraquinone sulphonates are described by Goldberg, J.C.S. 1931, 1771; *ibid.* 1931, 2829; *ibid.* 1932, 73; *ibid.* 1932, 83.

The nuclear syntheses of di-, tri-, and tetramethylanthraquinones from benzophenones and butadienes are described by Morgan, J.C.S. 1929, 2204, 2551.

A. A. G.

ANTHRAQUINONE DYESTUFFS.

I. Historical.
II. Acid Alizarin Colours.
III. Vat Colours.
  (*a*) Intermediates.
  (*b*) The Discovery of Indanthrone and Early Developments.

(*c*) Present Ranges of Vat Colours.
Indanthrone Derivatives.
Acylaminoanthraquinones.
Acridones.
Analogues of Indanthrone.
Pyranthrone and Flavanthrone.
Polyanthrimides.
Carbazole Dyestuffs.
Sulphurised Colours.
Dibenzanthrones.
Derivatives of other Homocyclic Quinones.
Perylene.
Recent Research.
Solubilised Vat Dyes.
Brilliancy of Shade.
Literature.

I. HISTORICAL.

The anthraquinone dyestuffs industry owes its inception in the first place to the alizarin industry, which, commencing about 1870, developed the chemistry of anthraquinone and its simple derivatives. Very important contributions were made at later dates from indigo research and other branches of dyestuff chemistry. First came a range of mordant dyes followed by valuable acid dyestuffs dyeing wool without mordants, and the period from 1894 to 1901 was particularly fruitful in this respect, chiefly in the hands of R. E. Schmidt of the Bayer Co. These dyes were characterised by much greater fastness to light than those hitherto available, but the most valuable products were restricted in shade to purple, blue and green, with the exception of one very fast range of reds. As might be expected there was very considerable competition among the largest colour-making firms in Germany in producing new types and in attempts to capture the largest share of the growing application of these faster colours to wool for dress goods, uniforms and carpets. The most important dyestuff of this class was, and possibly is still, *Alizarin Saphirol B* (I.G.) (*Solway Blue B* (I.C.I.)).

The next landmark was the discovery of Indanthrone by R. Bohn in 1901. This was probably a direct outcome of analogy from the indigo synthesis, as the first experiments consisted in the fusion of (2)-anthraquinonylglycine with caustic potash (Kränzlein, *see* Literature, p. 429). It was, however, found that the acetic acid residue was unnecessary and that 2 aminoanthraquinone itself on fusion with caustic potash gave a new blue dyestuff, having a curious resemblance to indigo, but yet differing from it in reactions and fastness properties. Indeed the latter, especially the light fastness, were so striking that it was soon realised that a new standard of colour fastness for cotton had been set up.

The discovery of indanthrone gave a wonderful stimulus to research in anthraquinone chemistry, much assisted by the academic researches of Prof. Roland Scholl and F. Ullmann, and a range of vat dyes of a high degree of fastness was soon available. The application of this fast dye range to cotton attracted rapidly increasing attention, but had not attained to more than a few per cent. of the total consumption of dyes at the outbreak of war in 1914. At the present time, however, the total consumption of anthraquinone vat colours is 25% of the total of all dyestuffs and is valued at about £10,000,000 per annum (Kunz, *see* Literature, p. 429). This large increase is due to a combination of factors. It results from a demand for faster colours by the gradual education of the consumer to a higher standard of requirements, from the textile manufacturer's desire for colour which will survive for the useful life of the fabric he has constructed, and by the constant and sustained efforts of the main dye-producing firms to attain faster colours combined with increased brilliancy of hue and to widen the range of shades available.

It is convenient here to indicate the main landmarks of discovery which have been passed on the way during the period from 1894 to the present time :

Dyestuff.	Date of discovery.	Inventor.
Alizarin Blue Black ,, Cyanine Green ,, Saphirol	1894–1897	R. E. Schmidt (Bayer).
Indanthrone and Flavanthrone	1901	Bohn (Badische).
Dibenzanthrone and *iso*Dibenzanthrone	1904	Bally and Isler (Badische).
Caledon Jade Green	1920	Davies, Fraser Thomson, and Thomas (Scottish Dyes).
The Indigosols	1924	Bader and Sunder (Durand and Huguenin).
The Soledon Colours	1924	Jones, Harris, Wylam, and Thomas (Scottish Dyes).

The technical developments prior to the Great War took place almost entirely in Germany and were chiefly shared by the two largest companies, Bayer and Badische, and to a lesser extent by Meister, Lucius and Brüning, and Cassella. As would be expected, there was great rivalry.

The discovery of Indanthrone and Flavanthrone by Bohn in 1901 was within a short time followed by a period of fierce competition, supported by many important inventions on both sides, resulting in the *Indanthrene* range of dyestuffs (Badische) and the *Algol* colours (Bayer).

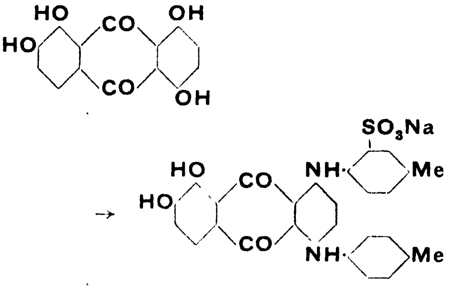
The outbreak of the Great War suspended these great research activities and gave rise to the resuscitation of the British dyestuffs industry and to considerably increased activity in Switzerland. British chemists, in spite of their chief efforts being at first imitative, have already been responsible for a number of important discoveries in anthraquinone dye chemistry,[1] including two of the last three items in the list given above. There has been a period of intense research activity in the field since the War in the chief European producing countries, and in America. Japan and Russia are beginning to enter the arena also, but have not yet left their mark on it.

The further development of anthraquinone chemistry is now proceeding at a less furious pace, as most of the obvious avenues have been partly explored. The trade is still growing, but at a slower rate, and this is partly due to competition from new and faster colours in other branches of dyestuff technology, particularly the azo class.

II. Acid Alizarin Colours.

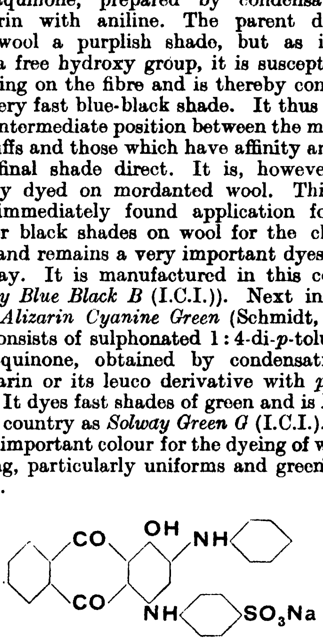
Owing their development to the alizarin industry, it is not surprising to find that the first new intermediates that became available were those derived either from alizarin itself or from the intermediates used in the manufacture of this dye. The introduction of a further hydroxyl group into alizarin (1 : 2-dihydroxyanthraquinone) by oxidation in various ways led to *purpurin* (1 : 2 : 4-trihydroxyanthraquinone), which was later reduced to *quinizarin* (1 : 4-dihydroxyanthraquinone). The sulphonation of anthraquinone, which originally gave nothing but the β-acids, namely, the 2-, 2 : 6-, and 2 : 7-, was found to take another course when catalysed with mercury salts, and yielded the 1-mono-, 1 : 5-, 1 : 8-, and to a lesser extent the mixed $\alpha : \beta$-disulphonic acids, the 1 : 6- and 1 : 7-. From these acids by fusion with lime water, the corresponding hydroxy bodies were easily prepared, of which the most important were the dihydroxyanthraquinones, *anthrarufin* (1 : 5) and *chrysazin* (1 : 8).

The early development of the acid alizarin colours is indissolubly linked with the name of R. E. Schmidt of the Bayer Co. This prolific inventor's first efforts were linked with those of Peter Bohn in the preparation of polyhydroxyanthraquinones derived from alizarin, by oxidation with sulphuric anhydride in presence of boric acid and catalysts (the Bohn-Schmidt reaction). These dyes, of course, all required mordants for fixation, but when it was discovered that *Alizarin Bordeaux* (1 : 4 : 5 : 6-tetrahydroxyanthraquinone) condensed with arylamines to yield a diarylaminodihydroxyanthraquinone which on sulphonation gave a green mordant dyestuff for wool (*Alizarin Viridine FF*) this reaction was extended to other hydroxyanthraquinones containing one pair of hydroxyls in the 1 : 4-positions.

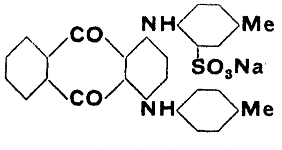


Alizarin Viridine FF (By).

The first of these to be discovered was *Alizarin Blue Black B* (Schmidt, 1894). This arose from the sulphonation of 2 : 4-dianilino-1-hydroxyanthraquinone, prepared by condensation of purpurin with aniline. The parent dyestuff dyes wool a purplish shade, but as it contains a free hydroxy group, it is susceptible to chroming on the fibre and is thereby converted to a very fast blue-black shade. It thus stands in an intermediate position between the mordant dyestuffs and those which have affinity and give their final shade direct. It is, however, frequently dyed on mordanted wool. This dyestuff immediately found application for fast grey or black shades on wool for the clothing trade and remains a very important dyestuff to this day. It is manufactured in this country (*Solway Blue Black B* (I.C.I.)). Next in order came *Alizarin Cyanine Green* (Schmidt, 1894). This consists of sulphonated 1 : 4-di-p-toluidinoanthraquinone, obtained by condensation of quinizarin or its leuco derivative with p-toluidine. It dyes fast shades of green and is known in this country as *Solway Green G* (I.C.I.). It is a very important colour for the dyeing of woollen clothing, particularly uniforms and green effect stripes.



Alizarin Blue Black B (By).

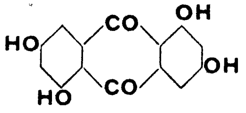


Alizarin Cyanine Green (By).

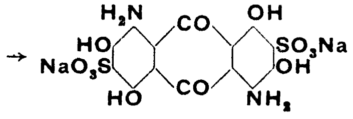
The 1 : 5- and 1 : 8-dihydroxyanthraquinones gave rise to the *Alizarin Saphirols* by a different type of process (Schmidt, 1897). The basic intermediate is sulphonated, nitrated, and reduced, a process which in 1892 had in the hands of Laubmann given a mordant-dyestuff from anthrachrysone (1 : 3 : 5 : 7-tetrahydroxyanthraquinone). (*Acid Alizarin Blue GR.*)

---

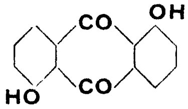
[1] A further contribution was the application of aminoanthraquinones to cellulose acetate (see **Acetate Silk Dyes**, p. 39).



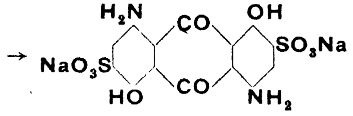
Anthrachrysone.



Acid Alizarin Blue GR (MLB).



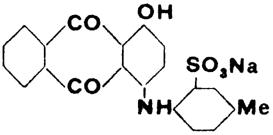
Anthrarufin.



Alizarin Saphirol B (By)
(*Solway Blue B* (I.C.I.)).

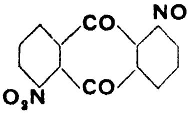
In the latter case a bright blue dyestuff is obtained, of particularly easy application, and although not quite fast to perspiration and sea-water and poor to milling, has become a very important dyestuff for carpet yarn and for woollen clothing of all descriptions, being very fast to light. In this dyestuff the sulphonic acid groups are attached to the anthraquinone itself, instead of to the pendent aryl groups. It is not suitable for chroming. The *SE* brand consists of the monosulphonic acid, obtained by reduction of the parent *B* brand. It is faster but less readily applied owing to its lower solubility.

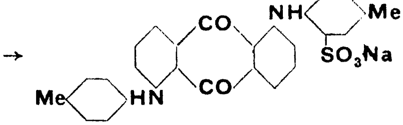
In the preparation of Alizarin Cyanine Green conditions can be devised for stopping the condensation at the half-way stage. This gives rise to the bright purple dyestuff *Alizarin Irisol R* (Schmidt, 1894); *Solway Purple R* (I.C.I.).



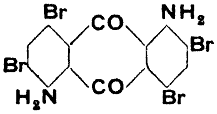
Alizarin Irisol R (By).

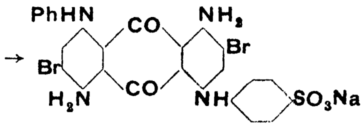
After this period, which, owing to Schmidt's inventions, was very fruitful for the Bayer Company, the Badische Company entered the field in 1898 with *Anthraquinone Violet* (1 : 5-di-*p*-toluidinoanthraquinone, sulphonated) and *Blue SR* (Bally). The former was obtained by condensing 1 : 5-dinitroanthraquinone with *p*-toluidine followed by sulphonation. The latter was obtained by tetrabromination of 1 : 5-diaminoanthraquinone, condensation with aniline and sulphonation :





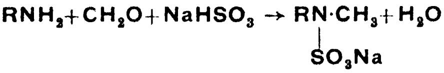
Anthraquinone Violet (B).





Anthraquinone Blue SR (B).

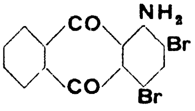
In 1899 Schmidt was responsible for *Alizarin Celestol R*, which was probably the reaction product when *Alizarin Saphirol B* or *SE* was treated with formaldehyde and sodium bisulphite, resulting in the formation of ω-methylaminosulphonic acids :



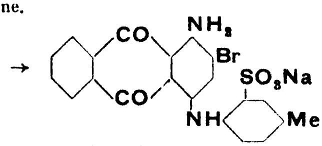
$$RNH_2 + CH_2O + NaHSO_3 \rightarrow \underset{\substack{| \\ SO_3Na}}{RN}\cdot CH_3 + H_2O$$

These developments were rapidly followed by another series derived from halogenated amino- or alkylaminoanthraquinones by condensation with arylamines, followed by sulphonation in the pendent aryl groups.

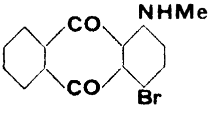
Examples of these are as follows :



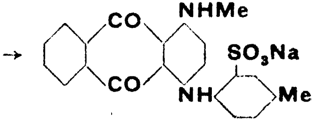
2 : 4-Dibromo-1-aminoanthraquinone.



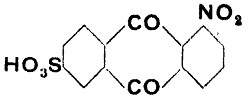
Alizarin Sky Blue B (Schmidt, 1899)
(*Solway Sky Blue B* (I.C I.)).



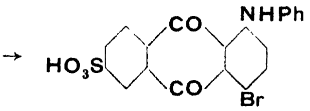
4-Bromo-1-methylaminoanthraquinone.

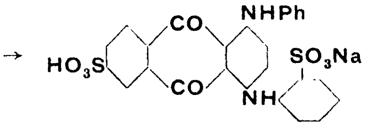


Alizarin Astrol B (Schmidt, 1901)
(*Solway Celestol B* (I.C.I.)).

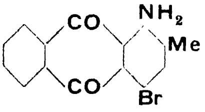


1-Nitroanthraquinone-6-sulphonic acid.

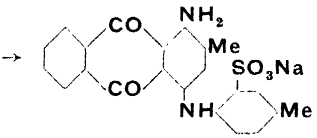




Anthraquinone Green GX (B) (Bally, 1900).

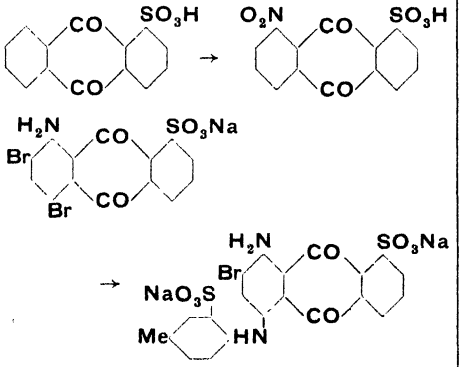


4-Bromo-1-amino-2-methylanthraquinone.



Cyananthrol R (B, 1900) (*Solway Blue R* (I.C.I.)).

While the greatest number of the trade dyestuffs are sulphonated in the pendent aryl groups, *Alizarin Saphirol B* and *Anthraquinone Green GX* are examples of dyestuffs having nuclear sulphonic acid groups. Another type dating from 1903 is *Alizarin Direct Blue B*. This was obtained by nitration, reduction, and bromination of anthraquinone-1-sulphonic acid, followed by condensation with *p*-toluidine and further sulphonation.

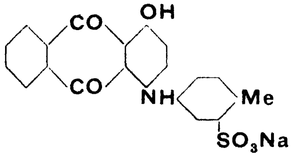


Alizarin Direct Blue B (MLB, Hepp., 1903).

About this time a series of alternative syntheses of these types were carried out by Meister, Lucius and Brüning, and Cassella. The variation consisted in condensing an arylamine sulphonic acid with the hydroxy or halogenated anthraquinone. As a rule, therefore, a metasulphonated arylamine was used and this led to dyestuffs isomeric with those produced by direct sulphonation.

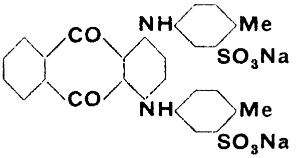
Examples are :

Leucoquinizarin + 4 - aminotoluene- 2 -sulphonic acid (1 mol.)—



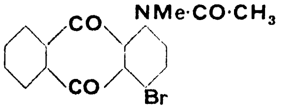
Alizarin Direct Violet R (MLB, 1903). (Compare Alizarin Irisol R.)

As above + 2 mols.—

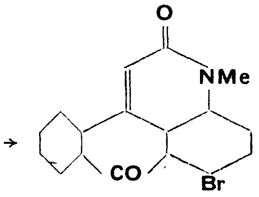


Alizarin Direct Green G (MLB, 1903). (Compare Alizarin Cyanine Green.)

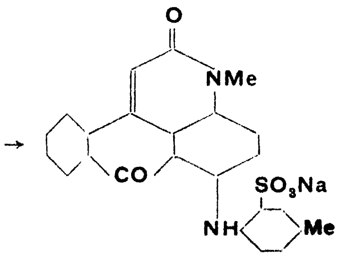
A valuable fast red is obtained if 4-bromo-1-methylaminoanthraquinone is acetylated and dehydrated to the anthrapyridone in caustic soda suspension, followed by the usual arylamine condensation and sulphonation. This is *Alizarin Rubinol R* (*Solway Rubinol R* (I.C.I.)).



4-Bromo-1-methylacetaminoanthraquinone.

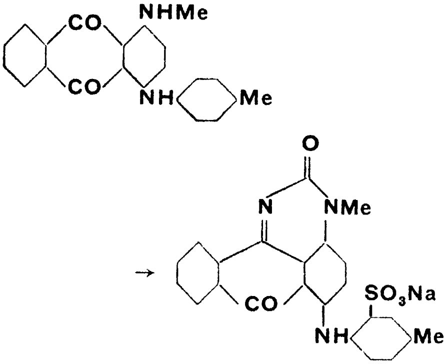


4-Bromo-1-*N*-methylanthrapyridone.



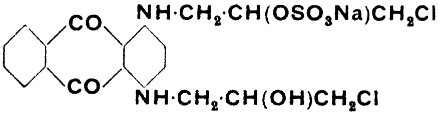
Alizarin Rubinol R (By) (*Solway Rubinol R* (I.C.I.)).

Alizarin Geranol B is a somewhat similar dyestuff containing a pyrimidone nucleus. It is obtained by condensing 1-methylamino-4-*p*-toluidinoanthraquinone with urea and sulphonating.

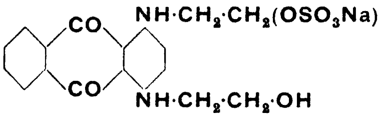


Alizarin Geranol B (By).

Particularly bright shades of blue are exhibited by the *Alizarin Uranols R* and *B* (Bayer, Berchelmann, 1910). These colours are derived by the condensation of 1 : 4-diaminoanthraquinone with epichlorohydrin or ethylene oxide under very mild conditions, followed by gentle treatment with sulphuric acid. The dyestuffs are probably oxygen sulphuric esters.

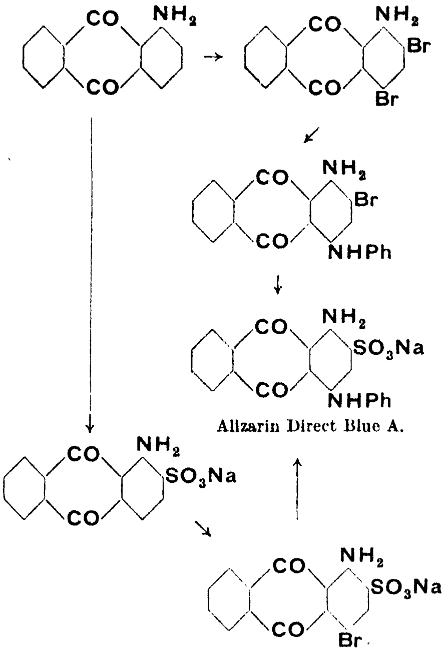


Alizarin Uranol R.



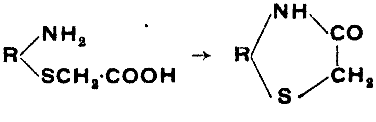
Alizarin Uranol B.

Since the Great War a number of new types have become important in addition to the older colours, which in spite of their light fastness have in general only moderate fastness to milling and washing. An improvement in this direction was obtained with *Alizarin Direct Blue A* (*Solway Ultra Blue B* (I.C.I.)), which contains a nuclear 2-sulphonic acid grouping, a free 1-amino group, and also an aniline residue in the 4-position. This colour is derived in several ways from 1-aminoanthraquinone. The latter may be brominated to the 2 : 4-dibromo-derivative, condensed with aniline, and the remaining 2-bromine atom replaced by a sulphonic acid group by heating under pressure with sodium sulphite. Alternatively, by baking the acid sulphate of 1-aminoanthraquinone, the 2-sulphonic acid is produced, and this, in aqueous solution, brominates to the 4-bromo-derivative. Condensation with aniline proceeds in the same medium, yielding the dyestuff.



Alizarin Direct Blue A.

The intermediate sodium 4-bromo-1-aminoanthraquinone-2 sulphonate has an extremely active bromine atom, which reacts readily in aqueous solution. From this source a range of dyes has been prepared, some of which are important either for improved fastness to milling or increased brightness. Bright shades are usually obtained when alkyl groups only are attached to the nitrogen of the 4-amino group, but these are often deficient in light fastness. The latter is improved by aryl groups. Several interesting new types have been mentioned in recent literature. Colours fast to light and of good levelling properties are the *Anthralan* colours (I.G.), while other ranges are in course of development. The properties sought in these are (*a*) a range of colours to stand mild washing treatment, of good levelling and fastness to water, (*b*) fast milling colours. Among the latter may be noted the lactam type of anthraquinone wool dyes (Soc. Chem. Ind., Annual Reports on the Progress of Applied Chemistry, 1933, p. 126) (I.C.I.). The principle involved here is the dyeing of the fibre with *o*-aminothioglycollic acids derived from anthraquinone, the lactam being formed on the fibre during dyeing and resulting in very fast dyes.

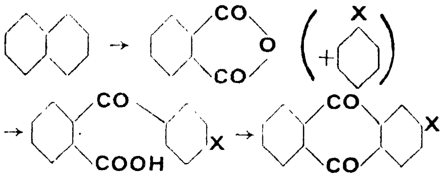


III. Vat Colours.

(a) Intermediates.

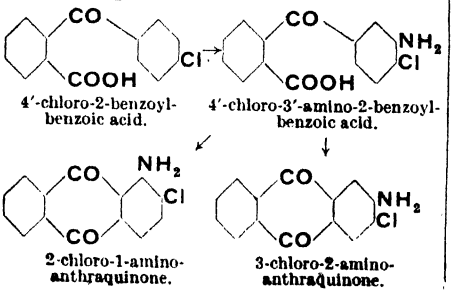
The tremendous impetus given to research by the success of the acid alizarin colours in the last decade of the nineteenth century led to a vast increase in knowledge of anthraquinone chemistry and to the building up of a wide range of intermediate products, each having its application as the basis of new colours. It is intended here briefly to show the inter-relation of these products.

1. Routes to Anthraquinone.—Two main routes to anthraquinone and its derivatives exist: (*a*) *via* coal-tar anthracene and oxidation; (*b*) *via* naphthalene, by oxidation to phthalic anhydride and either Friedel-Crafts condensation with aromatic hydrocarbons and elimination of water, or sulphuric acid condensation with phenol derivatives. The first route only yields anthraquinone itself, but the Friedel-Crafts is a general method and is essential for preparation of a variety of β-substituted anthraquinones, while the sulphuric acid method is restricted to certain hydroxyanthraquinones. With monosubstituted benzene hydrocarbons the Friedel-Crafts condensation proceeds in the *para*-position entirely, leading to 2-benzoylbenzoic acids substituted in the 4′-position and hence by loss of water to 2-substituted anthraquinones:



The 2-chloro- and 2-methylanthraquinones are manufactured in this way, and in countries short of anthracene, for instance in the United States, the method becomes of importance for anthraquinone itself. The sulphuric acid method is chiefly important for quinizarin and is referred to later.

The intermediate 2-benzoylbenzoic acids can be further substituted, *e.g.* by nitration and reduction, and this method, starting with 4′-chloro-2-benzoylbenzoic acid, is a source of pure 3-chloro-2-aminoanthraquinone and of 2-chloro-1-aminoanthraquinone, which is simultaneously formed during ring-closure. These compounds are separated according to Scottish Dyes (B.P. 264916) by their different solubilities in strong sulphuric acid.



4′-chloro-2-benzoyl-benzoic acid.

4′-chloro-3′-amino-2-benzoyl-benzoic acid.

2-chloro-1-amino-anthraquinone.

3-chloro-2-amino-anthraquinone.

Phthalic anhydride was formerly manufactured on a large scale in Germany for indigo synthesis by oxidation of naphthalene with sulphuric anhydride in presence of a mercury catalyst. It is now everywhere prepared by the catalytic air-oxidation of naphthalene in continuous plant by a process independently developed by Gibbs in America and Wahl in Germany. This method yields a product of high purity and in good yield, and it finds increasing application in the synthetic resin industry in addition to its use for anthraquinone derivatives.

2. Anthraquinone Sulphonic Acids.—The β-sulphonic acids of anthraquinone became well known in the development of the alizarin industry and include the 2-sulphonic acid and the 2 : 6- and 2 : 7-disulphonic acids. The use of a mercury catalyst changes the orientation and yields the 1-sulphonic acid and the 1 : 5- and 1 : 8-disulphonic acids, in addition to smaller amounts of the 1 : 6- and 1 : 7-disulphonic acids.

It is interesting to note that the mercury catalyst can be used in desulphonation and by heating in about 80% sulphuric acid any α-sulphonic acid group can thereby be eliminated. In this way the 1-sulphonic acid and the 1 : 5- and 1 : 8-disulphonic acids yield anthraquinone, while the 1 : 6- and 1 : 7-disulphonic acids yield the 2-sulphonic acid.

3. Monosubstituted Anthraquinones.—The monosubstituted anthraquinones each exist as two isomers, the α and β. These are mostly prepared from the 1- and 2-sulphonic acids respectively, the most important in the case of the α-series being the amino- and methylamino-derivatives, prepared by heating under moderate pressure with ammonia or methylamine in presence of an oxidising agent. In the β-series 2-aminoanthraquinone is formed by high-pressure treatment of the 2-sulphonic acid with ammonia and an oxidising agent. The oxidising agent is required in these processes to prevent the sulphite formed in the substitution reacting, under the prevailing alkaline conditions, on the carbonyl groups, as this leads to loss in yield by reduction.

The α-sulphonic acids also react readily with methanol and alkali, yielding the α-methoxy derivatives, of which 1-methoxyanthraquinone is of some importance. They also readily yield the α-chloro derivatives in weak hydrochloric acid solution in presence of sodium chlorate; the β-sulphonic acids yield the β-chloro derivatives somewhat less readily.

Nitration of anthraquinone proceeds mainly in the α-positions, but it is difficult to stop the reaction at the 1-nitro stage and this reaction is not now of great technical importance. The 1 : 5-dinitro derivative can be isolated with some difficulty in a pure state and in the early developments was an important intermediate, but as the yield is only about 40% the process has now little economic significance. Nitration in certain cases works well, *e.g.* the nitration of 2-methyl- and of 1-methoxyanthraquinone, yielding the 1-nitro-2-methyl- and 1-methoxy-4-nitroanthraquinone respectively.

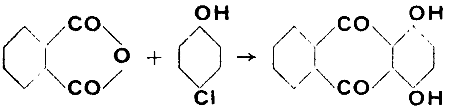
The 2-halogen- and 2-methylanthraquinones are prepared by the phthalic anhydride synthesis, the most important being 2-chloro- and 2-methylanthraquinone. The latter is oxidisable with difficulty to the 2-carboxylic acid, but when halogenated, yields chiefly 1-chloro-2-methylanthraquinone, which is more readily oxidised to 1-chloroanthraquinone-2-carboxylic acid.

The sulphonic acids readily yield the corresponding hydroxyl derivatives by lime fusion. Here again an oxidising agent is necessary to restrain the reducing action of the sulphite first formed in the substitution. The 1-hydroxy- and 2-hydroxyanthraquinones are very readily formed in this way, and the 1 : 5- (anthrarufin) fairly and the 1 : 8-dihydroxy (chrysazin) a little less readily.

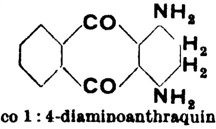
4. Disubstituted Anthraquinones.—In this case ten isomers are possible, viz. 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 6, 1 : 7, 1 : 8, 2 : 3, 2 : 6, 2 : 7, and 1 : 9. The last refers to cyclic compounds such as benzanthrone and anthrapyridone. The most important classes are the 1 : 4, 1 : 5, and 1 : 9, and to a lesser extent the 1 : 2, 2 : 3, 1 : 8, 2 : 6, and 1 : 6.

(*a*) 1 : 2-*derivatives*.—The chief representatives are 1-amino-2-methylanthraquinone, 2-chloro-1-aminoanthraquinone, and 1-chloroanthraquinone-2-carboxylic acid already referred to. 1-Chloro-2-aminoanthraquinone is of less importance and is the chief product of chlorination of 2-aminoanthraquinone. 2-Bromo-1-methylaminoanthraquinone is best prepared by methylation of 2-bromo-1-aminoanthraquinone.

(*b*) 1 : 4-*derivatives*.—This is perhaps the largest and most important class of substitution products of anthraquinone. The most important source is quinizarin, derived by condensation of phthalic anhydride with hydroquinone *or* *p*-chlorophenol in sulphuric acid solution, in presence of boric acid :

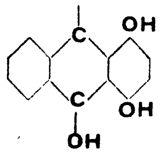


Quinizarin readily reduces to a leuco compound, which is very reactive. Thus with ammonia or methylamine under moderate pressure it yields leuco 1 : 4-diamino- or leuco 1 : 4-dimethyldiaminoanthraquinone respectively. These substances are now considered to be hydroaromatic, *e.g.*



Leuco 1 : 4-diaminoanthraquinone.

i.e. 2 : 3-dihydro-1 : 4-diaminoanthraquinone. Formerly they were considered to be reduced at the carbonyl groups :



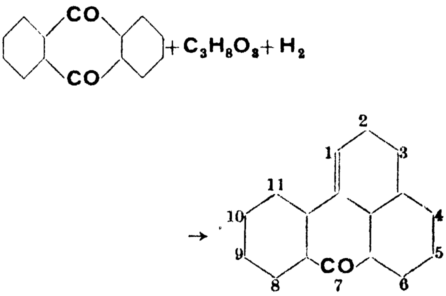
Leucoquinizarin (old formula).

Both leuco compounds yield the diamines on oxidation and the latter may have one methyl group removed by heating with sulphuric acid, thus yielding 1-amino-4-methylaminoanthraquinone.

1 : 4-diaminoanthraquinone can be mono- or di-acylated, *e.g.* to mono or dibenzoyldiaminoanthraquinone by choosing suitable conditions. 1-Hydroxyanthraquinone yields the 4-nitro derivative on nitration, reducing to 1-amino-4-hydroxyanthraquinone, and 1 methoxyanthraquinone nitrates particularly well, yielding after reduction very pure 1-amino-4-methoxyanthraquinone. 1-Chloro-4-aminoanthraquinone is less simply prepared, for instance, by chlorination of 1-benzoylaminoanthraquinone in acetic acid solution, followed by debenzoylation with sulphuric acid. Nitration is carried out in the same way, yielding eventually 1-nitro-4-aminoanthraquinone. 4-Bromo-1-methylaminoanthraquinone is formed exclusively by bromination of the 1-methylamino derivative.

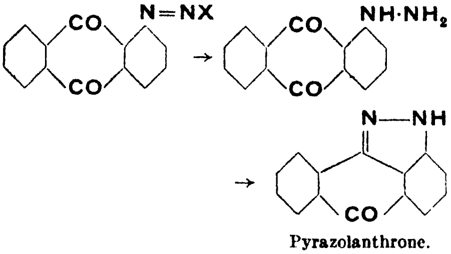
(*c*) 1 : 5-*derivatives*.—The chief source of these is the 1 : 5-disulphonic acid. It readily yields 1 : 5-dichloroanthraquinone, as already referred to. The latter may have its halogens replaced singly or simultaneously by ammonia or acid amides such as benzamide, phthalimide, or *p*-toluenesulphonamide, yielding after hydrolysis 1-chloro-5-amino- and 1 : 5-diaminoanthraquinone. Again, if the 1-sulphonic acid is nitrated it yields an easily separable mixture of the 1 : 5- and 1 : 8-nitrosulphonic acids, and these by the hydrochloric acid-chlorate process and reduction yield 1-chloro-5- or 8-aminoanthraquinone, thus offering alternative routes to these intermediates. Reference has already been made to anthrarufin.

(*d*) 1 : 9-*derivatives*.—The chief of these is benzanthrone. It is produced from anthraquinone and glycerol in strong sulphuric acid solution in presence of a reducing agent.

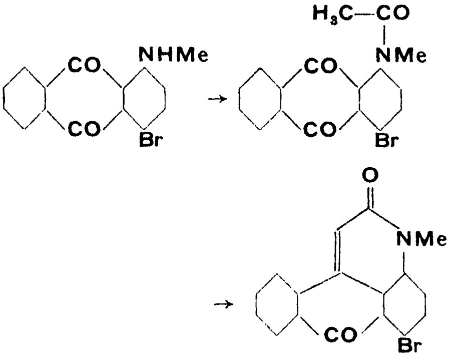


Benzanthrone.

There are a few other 1 : 9-derivatives of some interest. Pyrazolanthrone is produced by sulphuric acid dehydration of anthraquinone-1-hydrazine (produced either from diazotised 1-aminoanthraquinone by reduction or from 1-chloroanthraquinone by reaction with hydrazine or a salt of the latter and lime under pressure), and 4-bromo-1-*N*-methylanthrapyridone by dehydration in aqueous caustic alkali of 4-bromo-1-acetylmethylaminoanthraquinone :

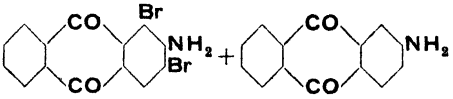


Pyrazolanthrone.

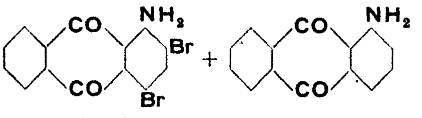


4-Bromo-1-*N*-methyl-anthrapyridone.

2 : 3-*derivatives.* — The chief representative here is the 3-chloro-2-aminoanthraquinone already referred to. 3-Bromo-2-aminoanthraquinone is prepared either by debromination of the 1 : 3-dibromo-2-amino derivative or by a curious reaction involving transference of labile bromine. The debromination may be accomplished by heating 1 : 3-dibromo-2-aminoanthraquinone in sulphuric acid solution with aniline. The migration is accomplished by heating together 1 molecular proportion each of 2-aminoanthraquinone and 1 : 3-dibromo-2-aminoanthraquinone in sulphuric acid. The 1-bromine atom then migrates to the unoccupied *β*-position and 2 molecular proportions of 3-bromo-2-aminoanthraquinone result. A similar reaction occurs with 1-aminoanthraquinone and its 2 : 4-dibromo derivative. The reaction product consists of 2-bromo-1-aminoanthraquinone.



→ 2 Mols. 3-bromo-2-aminoanthraquinone.



→ 2 Mols. 2-bromo-1-aminoanthraquinone.

1 : 8-*derivatives.*—Here the chief representative is the 1 : 8-dihydroxyanthraquinone (*chrysazin*) already referred to, but the 1 : 8-dichloro, obtained also from the 1 : 8-disulphonic acid, is also of some importance.

2 : 6-*derivatives.* — The 2 : 6-disulphonic acid yields the 2 : 6-dichloro and the 2 : 6-diaminoanthraquinone by the usual processes, and both intermediates have some applications.

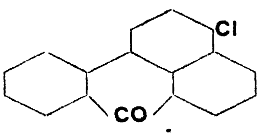
1 : 6-*derivatives.*—These are best obtained by nitration or halogenation of a *β*-substituted derivative, *e.g.* the 2-sulphonic acid. Thus the 1-nitro- and 1-amino-6-sulphonic acids are prepared.

4. Trisubstitution.—The chief isomers belong to the 1 : 2 : 4 and 1 : 4 : 5 classes. 2 : 4-Dibromo-1-aminoanthraquinone and 1 : 3-dibromo-2-aminoanthraquinone are formed by bromination of the corresponding amines and are important intermediates, as is also 1-bromo-3-chloro-2-aminoanthraquinone, prepared by bromination of 3-chloro-2-aminoanthraquinone. The 4-bromine in the 1 : 2 : 4-derivative can be transformed into hydroxyl by heating in sulphuric acid with boric acid. Similarly halogenation of the 2-sulphonic acid yields 1 : 4-dichloroanthraquinone-6-sulphonic acid. Nitration of 1 : 4-diaminoanthraquinone, after protecting the amino groups by an acid radical, yields 5-nitro-1 : 4-diamino- and hence the 1 : 4 : 5-triaminoanthraquinone, and this can also be obtained by a similar process from the 1 : 5- or 1 : 8-diaminoanthraquinones.

5. Tetrasubstitution.—1 : 4 : 5 : 8-Tetraminoanthraquinone is prepared by nitration and reduction of 1 : 5-diaminoanthraquinone, after suitable protection of the amino groups in the latter by an acid radical. The tetrachloro derivative may be prepared from the 1 : 5-dichloroanthraquinone by di-nitration followed by chlorination in a high-boiling solvent, which replaces the nitro groups by chlorine. Of some importance is 4 : 8-diaminoanthrarufin, obtained by nitration and reduction of a 1 : 5-dialkoxyanthraquinone. A convenient process is to nitrate the 1 : 5-diphenoxyanthraquinone, obtained by heating 1 : 5-dichloroanthraquinone with phenol. This introduces the necessary 4 : 8-nitro groups, as well as nitrating the phenol residues. The latter are then easily split off by means of caustic alkali, yielding 4 : 8-dinitroanthrarufin, which is reduced by the usual methods.

1 : 4-Diaminoanthraquinone on halogenation yields 2 : 3-dichloro-1 : 4-diaminoanthraquinone.

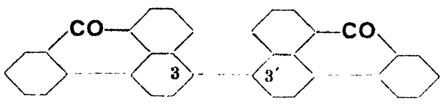
6. Benzanthrone Substitution Products.—The only important monosubstitution product is the 3-chlorobenzanthrone,



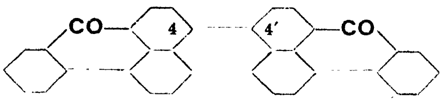
produced by chlorination of benzanthrone in a variety of ways.

More important are the dibenzanthronyls. 3 : 3′-Dibenzanthronyl is prepared by acid oxidation of benzanthrone in strong sulphuric acid with manganese dioxide, while 4 : 4′-

dibenzanthronyl results from mild alcoholic potash treatment.

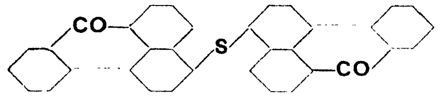


3 : 3′-Dibenzanthronyl.



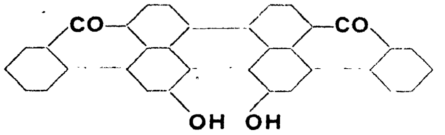
4 : 4′-Dibenzanthronyl.

The 3 : 3′-dibenzanthronyl sulphide (or alternatively selenide) is also of importance and is prepared from the 3-halogen derivative in an organic solvent by means of sulphur (or selenium) and an acid binding agent.



3 : 3′-Dibenzanthronyl sulphide.

3 : 3′-Dibenzanthronyl, on treatment with potash under mild conditions gives high yields of very pure dibenzanthrone. The latter on oxidation with manganese dioxide and sulphuric acid and mild reduction, or 4 : 4′-dibenzanthronyl under similar conditions, yields 2 : 2′-dihydroxydibenzanthrone.



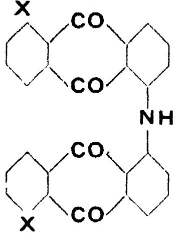
2 : 2′-Dihydroxydibenzanthrone.

The potash fusion of 3 : 3′-dibenzanthronyl sulphide (or selenide) gives high yields of very pure *iso*dibenzanthrone.

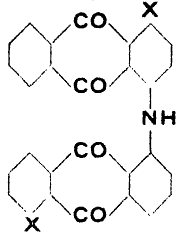
4-Methylbenzanthrone is of some technical importance. It is obtained as the main product when 2-methylanthraquinone is condensed with glycerol in strong sulphuric acid, in presence of a reducing agent.

7. Condensation of Two Anthraquinone Molecules.—1. *Anthrimides.*—Mono- or diaminoanthraquinones condense readily with chloro- or bromoanthraquinones in solvents in presence of an acid binding agent and a copper catalyst. In this way a very wide variety of anthrimides can be prepared, and the components may carry other substituents such as benzoylamino groups, or the latter may be introduced afterwards by nitration, reduction, and benzoylation. Several important examples are the 5 : 5′-dibenzoylamino-1 : 1′-dianthrimide (I), the 4 : 5′-dibenzoylamino-1 : 1′-dianthrimide (II), the 1 : 1′-dianthrimide (III), and the 1 : 1′, 4 : 1″-trianthrimide (IV).

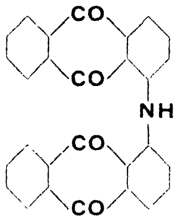
(—X = —NH·COPh.)



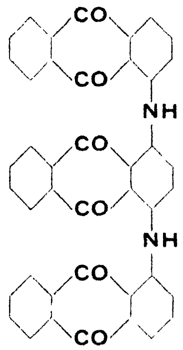
I.



II.



III.



IV.

III on nitration yields the 4 : 4′-dinitro derivative, which can be reduced and benzoylated and thus yields 4 : 4′-dibenzoylamino-1 : 1′-dianthrimide (V). I, II and V are the three possible isomers of the αα′-dibenzoylamino-dianthrimide type, excluding the 8 : 8′-substituents, examples of which are not used technically. The anthrimides especially of the α : β′- and β : β′-types are in a minority of cases themselves dyestuffs, but in the majority of cases, especially the α : α′-types, are further treated to yield dyestuffs.

2. *Dianthraquinonyls.*—These are produced by Ullmann's reaction, in which halogenoanthraquinones are heated with copper with or without solvents :

$$2RX+Cu \rightarrow R{-}R+CuX_2$$

The chief example is 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl.

(*b*) The Discovery of Indanthrone[1] and Early Developments.

By a vat dye is meant an insoluble pigment which in contact with an aqueous alkaline reducing agent passes into solution, yielding an alkali metal salt of a leuco compound, with affinity for cotton and other fibres, so that yarn or fabric steeped in the solution absorbs the leuco compound as the alkali salt and the latter can then be reconverted to the pigment by squeezing and oxidation in the air. In the case of the anthraquinone vat colours the leuco-compounds themselves are deeply coloured, differentiating them from the indigoids, the leuco-derivatives of which are generally colourless.

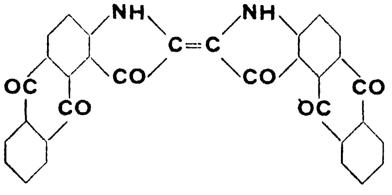
---

[1] The trade name *Indanthrene* was first given to this substance, but the ending *-one* is now preferred to indicate its quinonoid structure.

The friendly rivalry that existed between the large German dye firms in the period of the development of the acid alizarin colours had in several respects turned largely in favour of the products of the Bayer Co., for which, as has been seen, R. E. Schmidt was largely responsible. One can imagine that the chemists of the Badische Company must have longed sincerely for an outstanding new discovery which would cause the pendulum to swing in their favour.

Indigo and its derivatives were the only known family of vat dyes. Research had been proceeding in that field for the previous twenty years and a considerable degree of finality appeared to have been reached. The time was indeed ripe for a revolution in the dyeing of cotton. At the beginning of the century only comparatively few shades could be dyed on cotton with any degree of permanence to light and laundry. These were mainly the deep blues and reds obtained with indigo and alizarin, and fast pale shades were almost unknown. The public, with the exception of a minority, either treated the subject with apathy or regarded the problem as insoluble, while by some practical dyers the synthetic dyestuffs were still being compared unfavourably with the older products. The penetration of Western products to the East had reached almost its maximum and cotton was amongst the most important of our exports. In spite of this it was mostly exhibited to the tropical skies of India, China and other hot countries in shades of little permanence. The prevailing pale colours were almost as fleeting in the fogs, smoke and briny air of the home country.

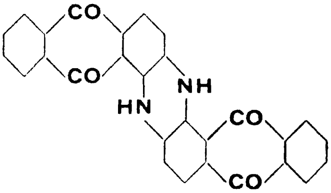
According to Kränzlein (*see* Literature, p. 429) indanthrone was first discovered by Bohn of the Badische Company when endeavouring to prepare an anthraquinone analogue of indigo. This was to be tried by applying the indigo potash fusion to (2)-anthraquinonylglycine instead of phenylglycine. This would presumably have led either to the compound I or an isomer of it.



4 : 5, 4′ : 5′-diphthaloylindigo.

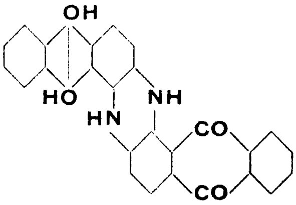
I.

However, it was soon found that the expected indigo formation did not occur, but that a blue dyestuff was formed from 2-aminoanthraquinone itself at about 200°C. without the necessity for condensing the latter with chloroacetic acid first. The preliminary work showed that by raising the fusion temperature the dyestuff became greener and at about 300°–350°C. the formation of a yellow dyestuff took place in noticeable quantities. It was found that the latter could be more economically produced by heating 2-aminoanthraquinone with aluminium chloride, or better still with antimony pentachloride in nitrobenzene solution. These dyestuffs were placed on the market in 1901 under the names Indanthrene and Flavanthrene, subsequently changed to ***Indanthrene Blue R*** and *Yellow G* respectively. The constitution of indanthrone was proved later, largely by the systematic work of Bohn and Scholl (Ber. 1903, **36**, 930, 3410, 3427, 3710 ; 1907, **40**, 320) to be N-*dihydro*-1 : 2′, 2 : 1′-*dianthraquinoneazine* (II).

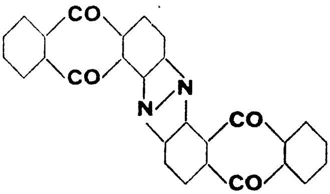


II.

Scholl also investigated the nature of the reduction products and showed that the compound normally present in the blue hyposulphite vat was the disodium salt of III, although a brown, completely reduced solution could be prepared by more vigorous methods.

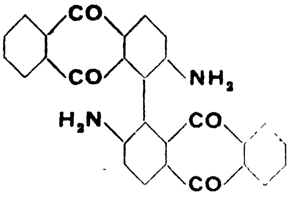


III.

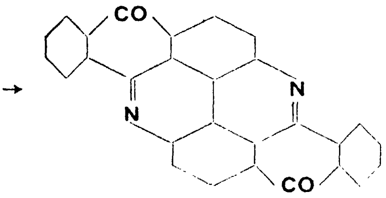


IV.

It was also noted that the azine (IV) was readily formed by the loss of the two hydrogens by oxidation, *e.g.* with hypochlorite, on the fibre. The azine is yellow, but is readily reduced again to the blue dihydroazine by treatment with alkaline hyposulphite. The constitution of Flavanthrone was demonstrated by Scholl (Ber. 1907, **40**, 1691 ; 1908, **41**, 2304 ; 1910, **43**, 1740) to be as follows (VI), and that the probable course of the reaction with antimony pentachloride in nitrobenzene is oxidative junction of two molecules through the 1-positions by loss of hydrogen (V), followed by dehydration of the resulting diaminodianthraquinonyl :

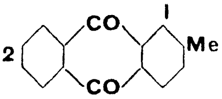


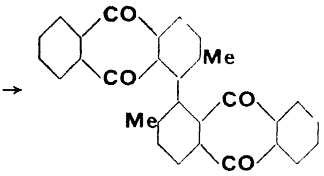
V.



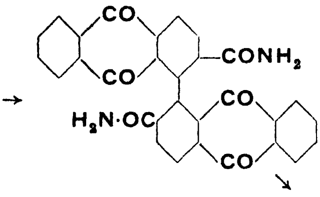
VI.

Synthesis confirmed this by the following route. 1-Iodo-2-methylanthraquinone prepared from 1-amino-2-methylanthraquinone, is converted to the dimethyldianthraquinonyl derivative (VII) by heating with copper. This on oxidation and treatment with ammonia gave the acid amide VIII, which on treatment by the Hofmann process passed into flavanthrone directly :



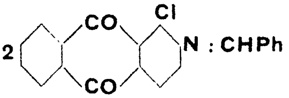


VII.

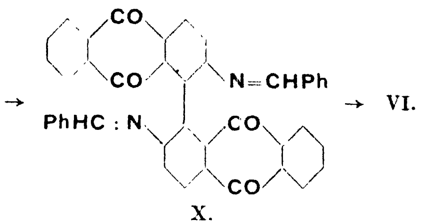


VIII. VI.

This synthesis was further confirmed later by Ullmann (D.R.P. 248999), who started with 1-chloro-2-aminoanthraquinone, preparing the benzylidene derivative (IX), heating the latter with copper to obtain the dianthraquinonyl derivative (X), and hence treating with sulphuric acid to give flavanthrone :

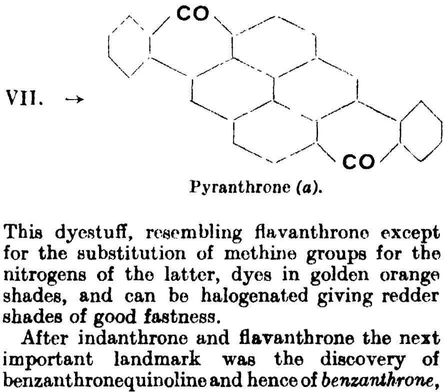


IX.



X.

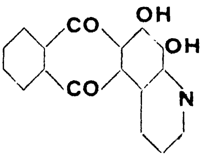
Arising out of the work on the synthesis of flavanthrone, *pyranthrone* was discovered by submitting 2 : 2′-dimethyl-1 . 1′-dianthraquinonyl to potash fusion (Scholl, Ber. 1910, **43**, 346 ; 1911, **44**, 1448) :



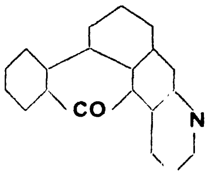
Pyranthrone (*a*).

This dyestuff, resembling flavanthrone except for the substitution of methine groups for the nitrogens of the latter, dyes in golden orange shades, and can be halogenated giving redder shades of good fastness.

After indanthrone and flavanthrone the next important landmark was the discovery of benzanthronequinoline and hence of *benzanthrone*, announced in 1904. When Skraup's quinoline synthesis, familiar in this series through the Alizarin Blue reaction with β-aminoalizarin, was carried out with 2-aminoanthraquinone and glycerol in 82% sulphuric acid, it was discovered that besides the usual pyridine ring formation, an additional benzene ring was formed (Bally, Ber. 1905, **38**, 194; Scholl, Ber. 1911, **44**, 1656).



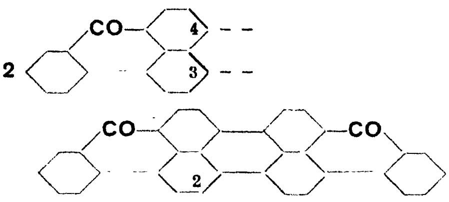
Alizarin Blue.



Benzanthronequinoline.

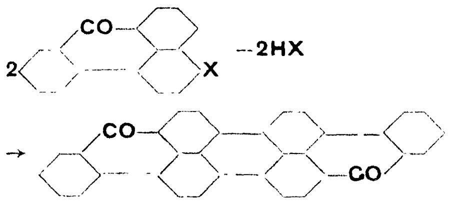
The formation of the additional benzene ring was seen to be a property of the quinone grouping when anthranol, or anthraquinone partly reduced by means of a metal, was condensed by the same method, and gave rise to benzanthrone.

Both benzanthrone and benzanthronequinoline have active hydrogens in positions 3 and 4. Thus caustic potash fusion was found to lead to the formation of *violanthrone* or *dibenzanthrone* by the oxidative junction of two molecules of benzanthrone :



Dibenzanthrone.

while halogenation of benzanthrone led to the 3-halogeno derivative, which on caustic alkali fusion gave rise to the isomeric dye, iso*violanthrone* or iso*dibenzanthrone* of redder and brighter shade, by loss of halogen acid :

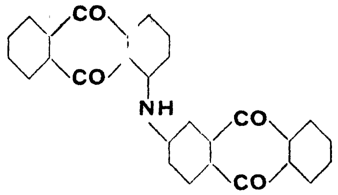


*iso*Dibenzanthrone (X).

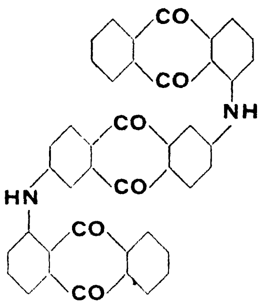
The halogenated derivatives of these two dyes also proved to be of interest, while dibenzanthrone on nitration yielded a mono-nitro derivative which on alkaline reduction in the dyebath gave an aminodibenzanthrone dyeing green shades. It is most probable that the nitro group is in the 2 position. The green on exposure or treatment with bleaching solution changed over to an intense fast black. The constitution of the latter is still unknown, but it is restored to the green again by hyposulphite reduction, suggesting a simple reaction of the type : $2RNH_2 \rightleftharpoons RNH{-}NHR$

The next important step was the discovery that while aminoanthraquinones were of no value as vat dyes as such, having no affinity, their α-aracyl derivatives, *e.g.* the α-benzoylaminoanthraquinones, possessed good affinity from a cold alkaline hyposulphite vat. The β-aracyl derivatives suffered from lack of tinctorial strength and affinity. The first of the former was *Algol Yellow WG* or 1-benzoylaminoanthraquinone (D.R.P. 225232, Helv. Chim. Acta, 1, 209), and a complete range from yellow to orange, red, blue and violet was developed by the Bayer Co., chiefly under the name of Deinet, by varying the constitution of the parent aminoanthraquinone by means of substituents (B.P. 2702, 1909).

The di- and trianthrimides were the next important class, formed by reaction between a chloroanthraquinone and an aminoanthraquinone. As the latter could have one or two amino groups, by using one or two molecules of the chloroanthraquinone a di- or trianthrimide resulted. The reverse method, using a dichloroanthraquinone, could also be used. Examples are :



Indanthrene Orange 6RTK (D.R.P. 174699, 208845).



Indanthrene Red G (D.R.P. 197554).

Here again there was a distinction, as the α : α′-dianthrimide type lacked affinity and depth of colour, only the α : β′ and β : β′ being of technical interest.

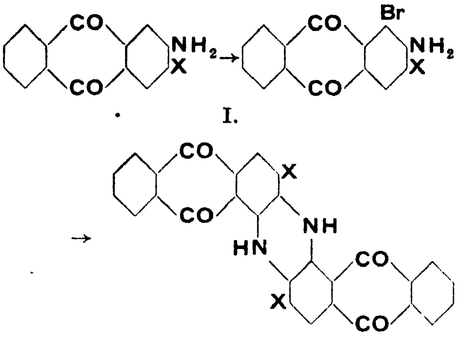
(c) Present Ranges of Vat Colours.

The manufacture of the anthraquinone vat dyes, which was confined to Germany before the Great War, has now spread to several important other sources. They are manufactured in this country and America, and in France, Switzerland and Italy, and to a lesser extent in Japan. Consequently, to avoid multiplicity of trade names in this article, from this point only the British names will be given in the case of dyes manufactured in this country. For correlation of trade names see the Colour Index of the Society of Dyers and Colourists (Rowe) and the latest edition of Schultz, "Farbstoff Tabellen."

Indanthrone Derivatives.

Indanthrone (*Caledon Blue RS, RNS*) has already been referred to. It is still one of the most important vat dyes, and its halogen derivatives are also of great importance. By direct chlorination of indanthrone, chlorination at first proceeds chiefly in the α (4 : 4′)-positions, with greening of the shade.

A monochloro- (*Caledon Blue GCP*), specially useful for printing (B.P. 23179, 1903), or a dichloro- (*Caledon Blue GCD*) or dibromo-derivative (*Caledon Blue GC*) can be thus prepared. Organic solvents or sulphuric acid as the medium and the free halogens or halogenating agents such as sulphuryl chloride can be used. On the other hand, halogen derivatives with the halogens in the 3 : 3′-positions (II) can be prepared synthetically from 3-halogeno-2-aminoanthraquinone by bromination to the 1-bromo-3-halogeno-2-aminoanthraquinones (I) followed by condensation of two molecules by means of an acid binding agent and a copper catalyst (B.P. 298248). They are markedly redder in shade, and similar in this respect to the parent indanthrone.



I.

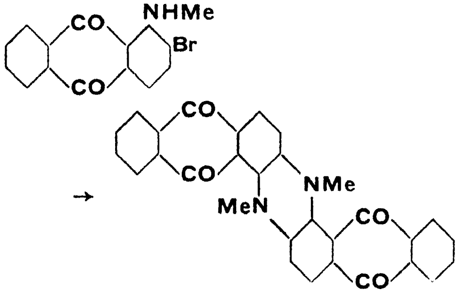
3 : 3′-Dihalogenoindanthrone.

II.

Of this type is *Caledon Blue RC*, and the tendency to oxidise to the yellow azine (*e.g.* on bleaching) is less marked in these cases, owing to the restraining influence of the *o*-halogen. *Indanthrene Blue BCS* (D.R.P. 331283) contains higher amounts of chlorine and is probably formed by direct halogenation. In this case the 3 : 3′-positions are partly substituted as well as the 4 : 4′, the halogen content exceeding that for a pure dichloro derivative.

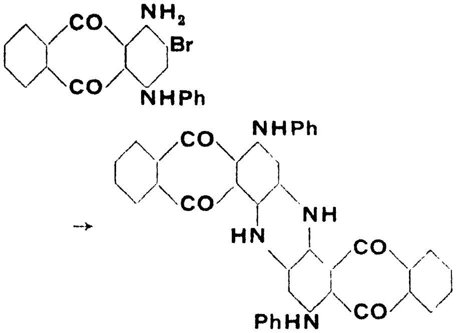
The *Brilliant Blues* (*Caledon Brilliant Blue RN*) are highly purified types of indanthrone itself. *Caledon Brilliant Blue 3G* (B.P. 23875, 1909) is a partly hydroxylated, partly sulphonated type produced by the action of sulphuric and boric acids on pure indanthrone, while *Indanthrene Blue 5G* (B.P. 7692, 1904) is the 4 : 4′-dihydroxy derivative, prepared from 1-bromo-2-amino-4-hydroxyanthraquinone by condensation of two molecules.

Caledon Green 2B (B.P. 7692, 1904) is the 3 : 3′-dichloro-4 : 4′-diaminoindanthrone prepared from 2 : 3-dichloro-1 : 4-diaminoanthraquinone by internal condensation. *Indanthrene Blue RK* (B.P. 7692, 1904 ; 17271, 1912), which dyes from a cold vat, consists of the *N*-dimethylindanthrone prepared from 2-bromo-1-methylaminoanthraquinone by self-condensation :



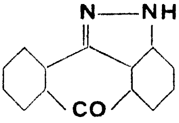
N-dimethylindanthrone.

It is rather surprising that this derivative is not faster to bleaching than indanthrone itself and yields a brown vat in the cold. *Caledon Green RC* consists of 4 : 4′-dianilinoindanthrone and is prepared from 2-bromo-1-amino-4-anilinoanthraquinone by self-condensation :

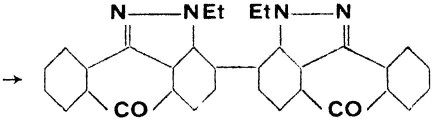


Caledon Green RC.

Flavanthrone has already been discussed. A dyestuff once thought to have a similar type of constitution is *Pyrazolanthrone Yellow*, which is not in itself an important dyestuff, as it contains two acidic hydrogens and so forms alkali metal salts. These can, however, be replaced by alkyl groups resulting in *Grelanone Scarlet* and *Anthra Rubine R* (I.G.). It is prepared from pyrazolanthrone by alkali fusion and alkylation, the scarlet being probably an intermediate product in the alkylation.

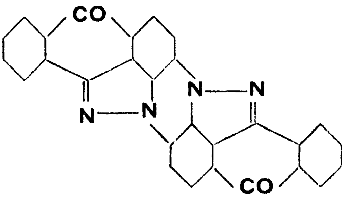


Pyrazolanthrone.

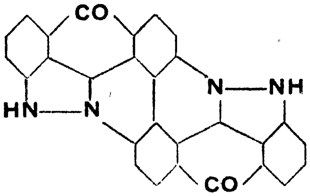


Anthra Rubine.

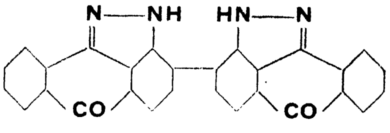
The structure of the dipyrazolanthrone has been variously proposed as III, IV, and V.



III. (Indanthrone type).



IV. (Flavanthrone type).



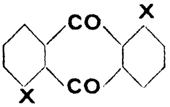
V. 2 : 2′-Dipyrazolanthronyl.

The first formula (III) does not account for the acidic hydrogens present, and the second formula (IV) was then proposed, but V has been proved to be the correct formula as the same body can be prepared from 2-bromo-1 : 9-pyrazolanthrone by the action of copper (U.S.P. 1817995). The latter intermediate is obtained from 2-bromo-1-aminoanthraquinone by diazotisation, careful reduction, and ring closure. Hence the correct name of V is 2 : 2′-dipyrazolanthronyl.

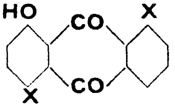
The indanthrone type III is obtained by self-condensation of the 2-bromo-1 : 9-pyrazolanthrone by means of copper and potassium acetate. The resulting red vat dyestuff gives a blue vat and possesses good fastness (B.P. 285555).

ACYLAMINOANTHRAQUINONES.—Of the very large range of acylaminoanthraquinones prepared and marketed as the *Algol Colours* by the Bayer Co. a limited number have survived. They are characterised by the presence of α-acylamino groups, as exclusively β-acylaminoanthraquinones are much weaker dyestuffs. Reference may be made to B.P. 2702 and 3055 (1909).

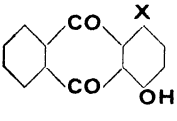
(X = —COPh.)



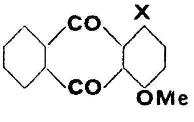
Caledon Yellow 3G.



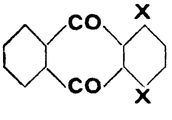
Caledon Red FF.



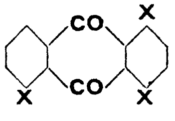
Algol Pink R.



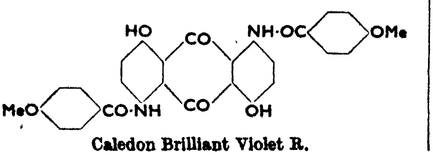
Algol Scarlet G.



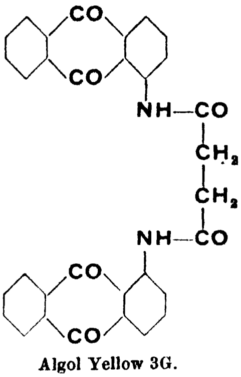
Caledon Red 5G.



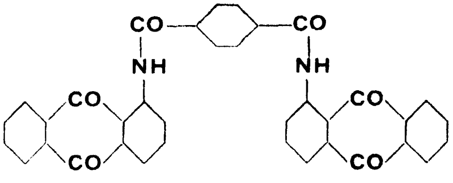
Caledon Red X5B.



Caledon Brilliant Violet R.



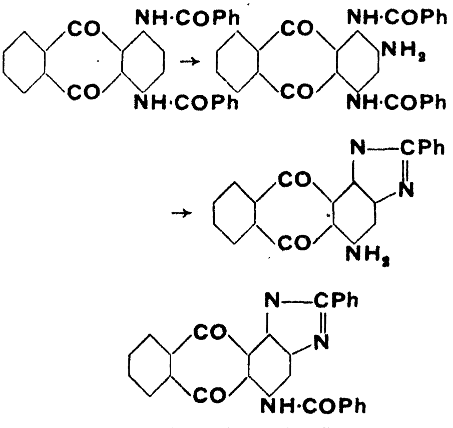
Algol Yellow 3G.



Paradone Yellow 5GK (H).

These dyes are all prepared by acylation of the appropriate intermediate by means of the chloride of the required acid.

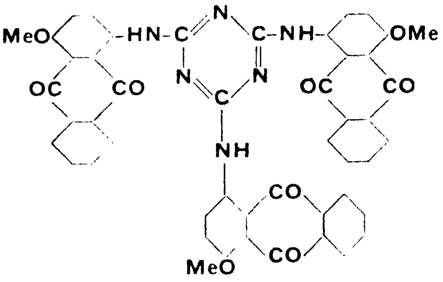
Another colour of this class, possessing a distinct structure is *Indanthrene Orange RRK*. This is prepared by benzoylating 1 : 4-diaminoanthraquinone, nitrating, and reducing. The amino compound forms the iminazole on treatment with sulphuric acid and is then rebenzoylated :



Indanthrene Orange RRK.

The benzoylaminoanthraquinones are characterised throughout by their property of dissolving in alkaline hyposulphite in the cold and, being very soluble in the vat, frequently require salt to promote exhaustion.

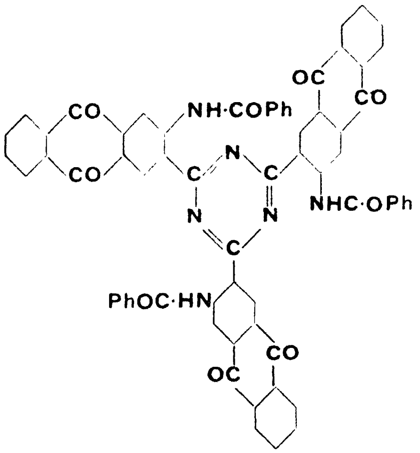
A valuable addition to the series has been made with *Cibanone Red 4B* and *Orange 6R* (S.C.I.B.), which belong to a class obtained by condensing aminoanthraquinones with cyanuric chloride of the type :



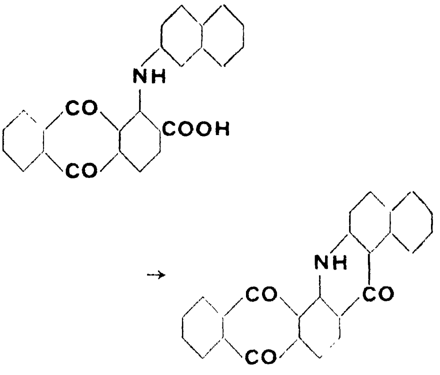
Cibanone Orange 6R.

With 1 : 4-diaminoanthraquinone a red-violet shade is obtained, or in presence of copper pure red, while 1-aminoanthraquinone gives a yellow and 1-amino-4-methoxyanthraquinone a red-orange (*Cibanone Orange 6R*) (S.C.I.B., D.R.P. 390201, 399485). *Cibanone Red 4B* belongs to the same class, and probably is a 1 : 4 derivative containing benzoylamino- groups.

A similar type, yielding orange shades, is given by another method of preparation used by the I.G., namely by heat polymerisation of cyanoaminoanthraquinones.

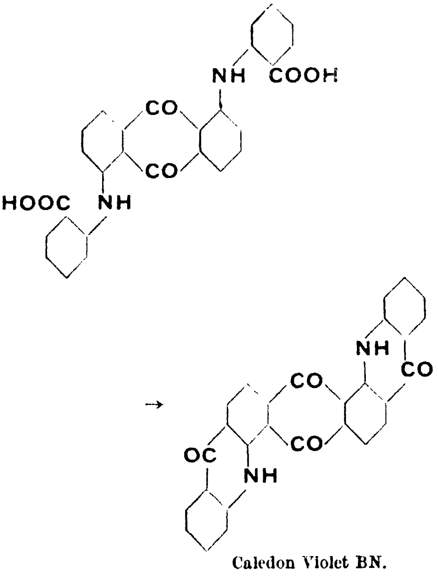


Acridones.—The acridones are a small class of colours which has not been substantially increased in number since the War. It contains colours of high light fastness, such as *Caledon Red BN*, *Violet BN*, and *Red Violet RRN*. *Caledon Red BN* is prepared by condensing 1-chloroanthraquinone-2-carboxylic acid with β-naphthylamine and ring-closing to the acridone by loss of water (B.P. 894, 1911 ; Ullmann and Bincer, Ber. 1916, **49**, 748).



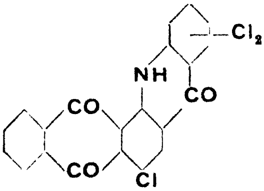
Caledon Red BN.

Caledon Violet XBN is prepared by condensing 1 : 5-dichloroanthraquinone with two molecules of anthranilic acid and ring closure (B.P. 12653, 1909 ; Ullmann and Ochsner, Annalen, 1911, **381**, 1, 10).



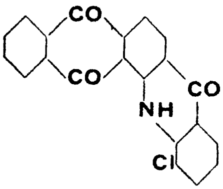
Caledon Violet BN.

Caledon Red Violet 2RN (B.P. 12653, 1909 ; Ullmann and Ochsner, Annalen, 1911, **381**, 1) is a chlorinated product obtained by simultaneous chlorination and ring-closure of 1-anilidoanthraquinone-2-carboxylic acid.

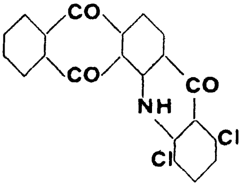


Caledon Red Violet 2RN.

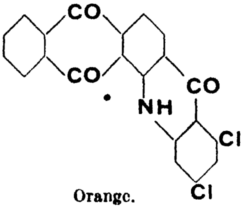
The position of the chlorine atoms is not determinate by this method. Of recent years much research has taken place on the effect on the colour of halogen atoms in different positions in the molecule, as shown by the following :



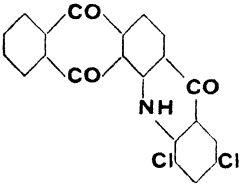
Bluish-red.



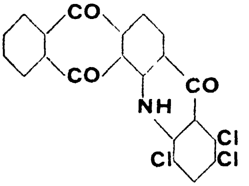
Scarlet.



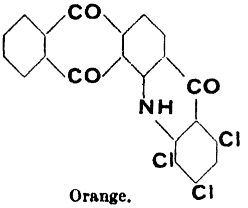
Orange.



Violet.



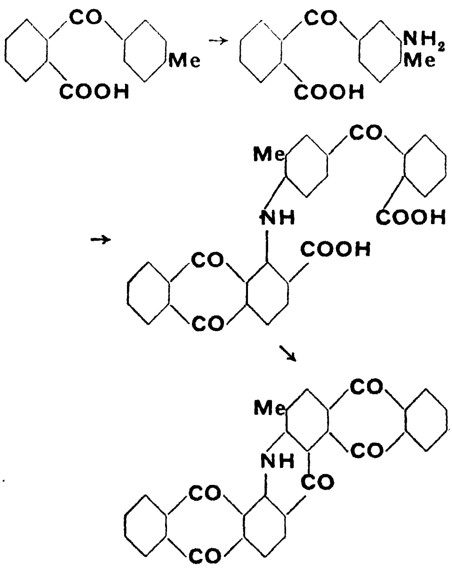
Scarlet.



Orange.

The effect of halogens in the anthraquinone itself has also been studied carefully. *Indanthrene Pink FBBL* is thought to belong to this class of dyestuff, and is claimed to combine increased brightness of shade with improved washing fastness. An amino group in the 4-position gives red-blue shades.

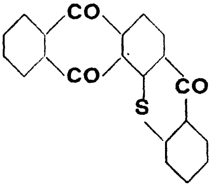
Indanthrene Orange F3R is a diphthaloylacridone which can be obtained by condensing 3′-amino-4′-methyl-2-benzoylbenzoic acid (obtained by nitration and reduction of 4′-methyl-2-benzoylbenzoic acid) with 1-chloroanthraquinone-2-carboxylic acid and double ring-closure :



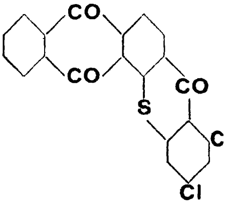
Indanthrene Orange F3R.

The acridones are useful dyestuffs, similar to the acylaminoanthraquinones in working from a cold vat and possessed therefore of good solubility and penetration, but while selected colours show high light fastness they are not of the highest washing fastness, nor are the reds capable of yielding very deep shades.

Similar to the acridones, but lighter in colour, are the *thioxanthones*. To this class belong *Indanthrene Gold Orange GN* and *Yellow GN extra*, the latter being a dichloro derivative of the former.



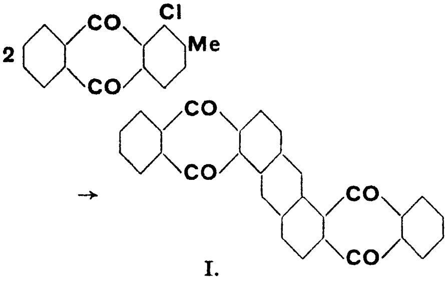
Indanthrene Gold Orange GN.



Indanthrene Yellow GN extra.

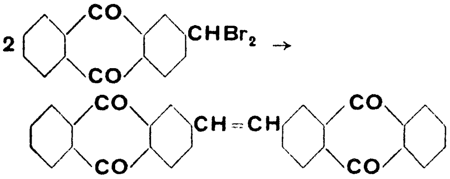
These colours are obtained by condensing 1-chloroanthraquinone-2-carboxylic acid with thiophenol and dichlorothiophenol respectively, followed by ring-closure with sulphuric acid (D.R.P. 243750, 258561).

Analogues of Indanthrone.—Since the value of indanthrone as a fast vat dyestuff was realised and its constitution known, various analogues have been prepared. All these are double molecules linked 1 : 2′ and 2 : 1′. The earliest dyestuff thought to belong to this class was *Algol Yellow GC* or *Anthraflavone G*, which can be prepared by oxidation of 1-chloro-2-methylanthraquinone with lead peroxide. This was at first thought to be the methine analogue (I) of indanthrone :



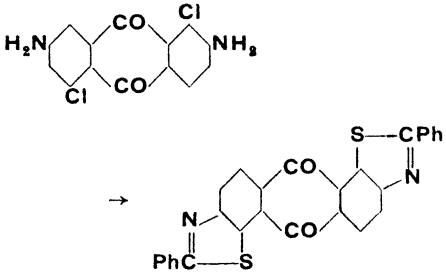
I.

Later preparations, however, were made from 2-dibromomethylanthraquinone by heating with copper, and this showed the dyestuff to consist of diphthaloylstilbene. This dyestuff is not of the highest light fastness and is not now in commerce (Ullmann and Klingenberg, Ber. 1913, **46**, 712).



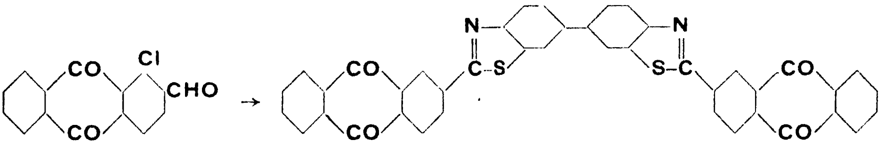
Anthraflavone G.

A much faster dyestuff of approximately similar greenish-yellow shade is *Paradone Yellow GC* (H.). This consists of anthraquinone 1:2, 5:6-ω-diphenylthiazole and is prepared from 1:5-dichloro-2:6-diaminoanthraquinone by condensation with benzaldehyde and sulphur :



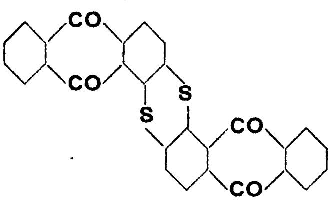
Paradone Yellow GC (H.).

A similar type of dyestuff is *Indanthrene Yellow GF*, which is considered by Fierz-David (J. Soc. Dyers, 1935, **51**, 50) to be a dithiazole derived from benzidine, sulphur, and anthraquinone-2-aldehyde or 2-methylanthraquinone.

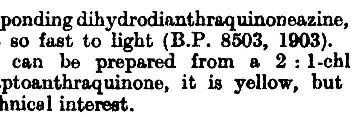


Indanthrene Yellow GF.

The oxygen and sulphur analogues of indanthrone have been prepared. The former is obtained from 1-chloro-2-hydroxyanthraquinone by fusion with sodium carbonate. It is yellow in colour and thus much lighter in shade than the corresponding dihydrodianthraquinoneazine, and is not so fast to light (B.P. 8503, 1903). The latter can be prepared from a 2 : 1-chloromercaptoanthraquinone, it is yellow, but not of technical interest.



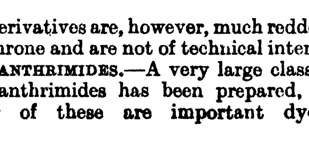
Erweco Fast Yellow G (W.)
Dianthraquinonylene dioxide.



Dianthraquinonedisulphide.

Pyranthrones and Flavanthrone.—*Pyranthrone* (*Caledon, Gold Orange G*) is still an important dyestuff, as are its dibromo- (*Orange RRT*) and tribromo- derivatives (*Orange 4R*). Its method of preparation has already been discussed (page 413).

Flavanthrone (*Caledon, Paradone Yellow G*), in spite of its poor washing fastness and rather inferior fastness to light, is also still of importance. Its 3:3′-dichloro- and dibromo-derivatives have been prepared from either 3-halogeno-2-aminoanthraquinone by the antimony pentachloride process, or from 1:3-dihalogeno-2-aminoanthraquinone by treatment with copper and dehydration :

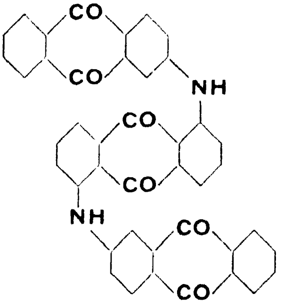


Dibromoflavanthrone (Alizanthrene Yellow R).

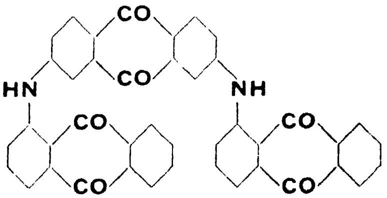
These derivatives are, however, much redder than flavanthrone and are not of technical interest.

Polyanthrimides.—A very large class of di- and trianthrimides has been prepared, and a number of these are important dyestuffs.

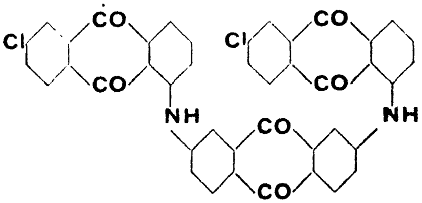
They are prepared by heating a mono- or dihalogenoanthraquinone with one or two molecules of an aminoanthraquinone in presence of an acid absorbing agent and a catalyst, or the inverse method may be employed, that is by taking a diaminoanthraquinone with two molecules of a halogenoanthraquinone. Examples of this type are *Indanthrene Orange 6RTK* (p. 414), which is 1 : 2′-dianthrimide, *Bordeaux B*, *Bordeaux extra Red R*, *Bordeaux 3B*, and *Algol Red BTK*. Usually only α : β- and β : β-dianthrimides are of technical interest, as the α : α types do not possess the necessary vatting behaviour and tinctorial strength. Exceptions are *Indanthrene Grey K* and, possibly, *Corinth RK*.



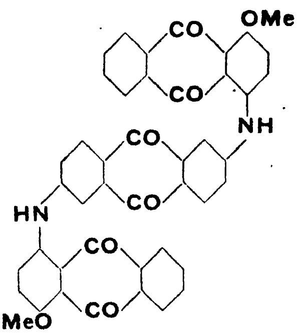
Indanthrene Bordeaux B (B.P. 10324, 1906).



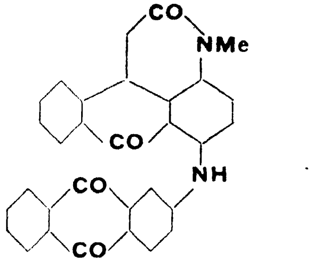
Indanthrene Red R (B.P. 4235, 1907).



Indanthrene Bordeaux B extra (B.P. 7418, 1908).



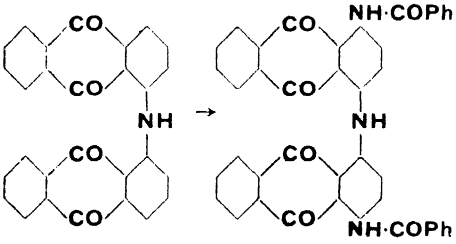
Algol Bordeaux 3B (B.P. 9219, 1909).



Algol Red BTK (B.P. 13686, 1907).

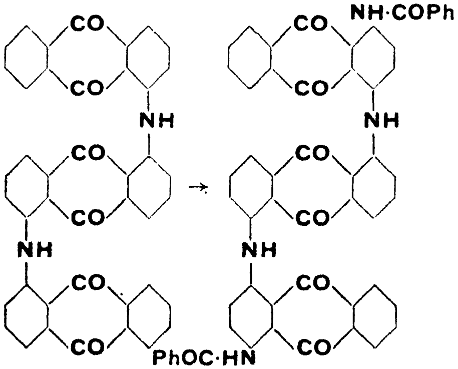
The mode of formation of these dyestuffs is clear from the formulæ. The last in the list is obtained from 4-bromo-1-*N*-methylanthrapyridone and 2-aminoanthraquinone.

As stated above, further dyestuffs probably belonging to this class are *Indanthrene Grey K*, obtained by nitration, reduction, and benzoylation of 1 : 1′-dianthrimide, and *Indanthrene Corinth RK*, probably obtained by a similar process from 1 : 1′, 5 : 1″-trianthrimide.



1 : 1′-Dianthrimide.

Indanthrene Grey K (B.P. 2702, 1909).

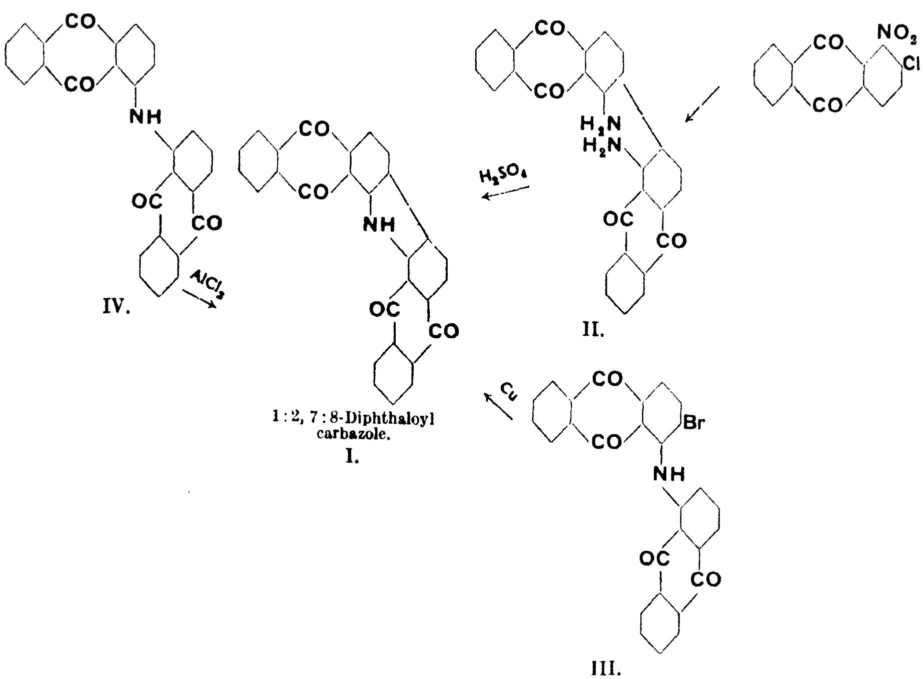


1 : 1′, 5 : 1″-Trianthrimide.

Indanthrene Corinth RK (D.R.P. 228992).

Carbazole Dyestuffs.—The dyestuffs of this class have the best average all-round fastness. Their chief mode of formation is by ring-closure of poly-α-anthrimides, with or without substituents, the latter usually being benzoylamino-groups. The simplest case is the treatment of 1 : 1′-dianthrimide (p. 411) with aluminium chloride, followed by hypochlorite treatment, yielding 1 : 2 : 7 : 8-diphthaloylcarbazole (I).

The constitution of this product, which dyes fast yellow shades from a red vat, has been established by two independent methods. 2-Chloro-1-nitroanthraquinone, by heating in nitrobenzene with copper, and reduction, yields 1 : 1'-diamino-2 : 2'-dianthraquinonyl (II), which splits off ammonia by means of sulphuric acid or zinc chloride to give (I), or alternatively 2-bromo-1-aminoanthraquinone is condensed with 1-chloroanthraquinone to give 2-bromo-1 : 1'-dianthrimide (III) followed by treatment with copper in nitrobenzene and yielding the same compound (I).



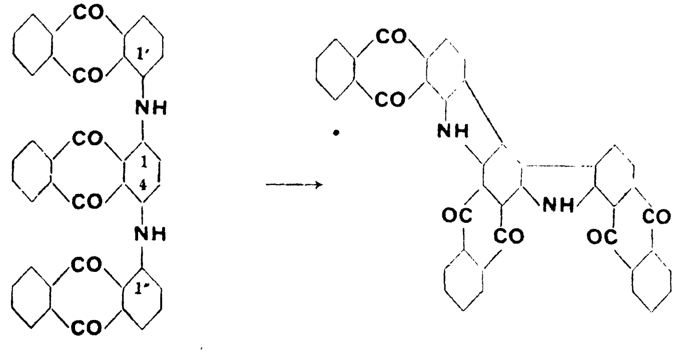
IV.

1 : 2, 7 : 8-Diphthaloyl carbazole.
I.

II.

III.

Before aluminium chloride became the common reagent for dehydrogenative ring-closure, potash fusion was occasionally employed, *e.g.* for trianthrimides. Thus *Indanthrene Brown GR* was derived in this way from the 1 : 1', 4 : 1''-trianthrimide.

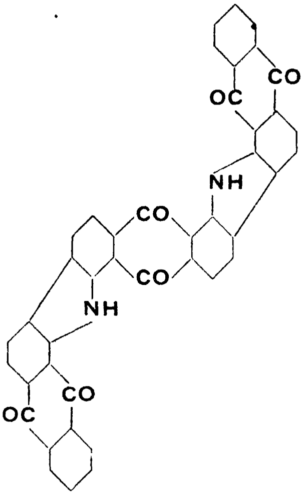


1 : 1', 4 : 1''-Trianthrimide.

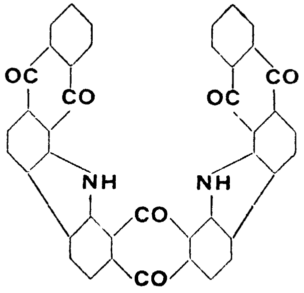
Indanthrene Brown GR (B.P. 25551, 1908).

Indanthrene Brown BR is a more recent type of the same dyestuff in a purer form, and is derived from the same intermediate by the improved method of ring-closure.

Sodium-aluminium chloride is very often used as the fusion medium to obtain fluidity at a lower temperature. In this way *Indanthrene Yellow 3RT* is derived from 1 : 1', 5 : 1''-trianthrimide and *Indanthrene Yellow 3R* from the 1 : 1', 8 : 1''-trianthrimide.

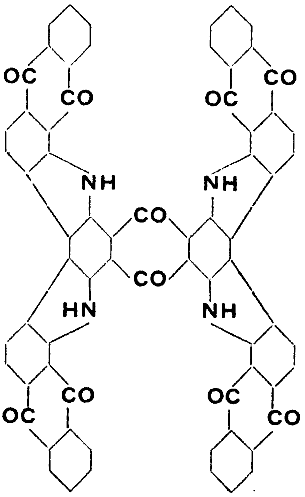


Indanthrene Yellow 3RT.



Indanthrene Yellow 3R.

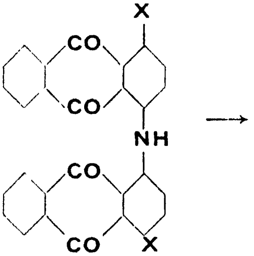
A still more complicated dyestuff is *Indanthrene Khaki 2G*, which is probably derived from the 1 : 1′, 4 : 1″, 5 : 1‴, 8 : 1⁗ (or more simply α-) pentanthrimide :



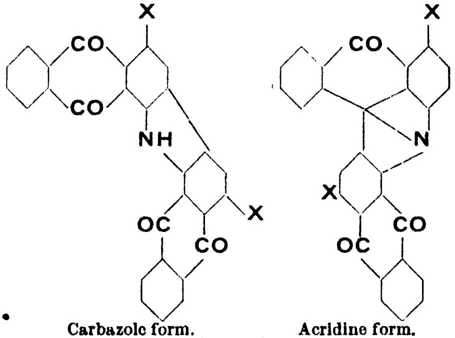
Indanthrene Khaki 2G.

In all these cases, after ring-closure, an oxidative bleaching treatment is required in order to develop the pure shade of the dyestuff, but the nature of this final stage of the reaction is not clearly understood. When the anthrimides contain benzoylamino-groups in α-positions ring-closure sometimes occurs much more readily, for instance with cold sulphuric acid. The dyestuffs in these cases were originally considered to be acridines formed by splitting off water, but their chemical behaviour and tinctorial properties are so similar to those of the carbazole dyes that they are now regarded as belonging to the latter class. The dyestuffs derived from three of the four possible α-dibenzoylamino-1 : 1′-dianthrimides, viz. *Caledon Olive R*, *Brown R*, and *Gold Orange 3G*, arising respectively from 4 : 4′-dibenzoylamino-, 4 : 5′-dibenzoylamino-, and 5 : 5′-dibenzoylamino-1 : 1′-dianthrimides (p. 411) by sulphuric acid ring-closure and bleaching are included in this section.

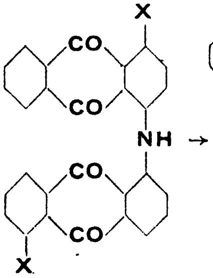
(—X = —NH·COPh.)



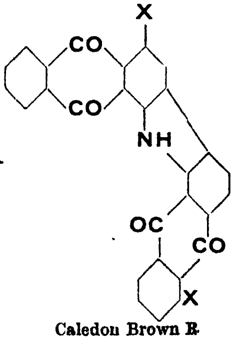
4 : 4′-Dibenzoylamino-1 : 1′-dianthrimide.



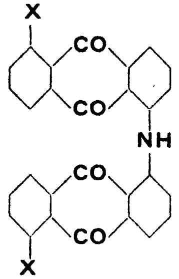
Carbazole form. Acridine form.
Caledon Olive R.



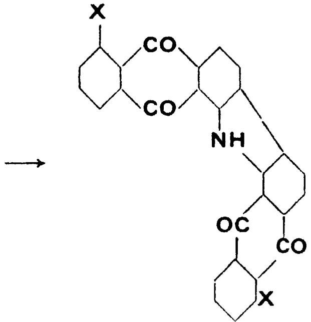
4 : 5′-Dibenzoylamino-1 : 1′-dianthrimide.



Caledon Brown R.



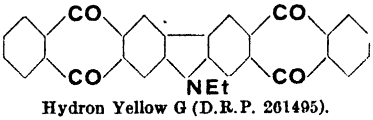
5 : 5′-Dibenzoylamino-1 : 1′-dianthrimide.



Caledon Gold Orange 3G.

One factor which comes into play in the anthrimide and carbazole dyestuffs is the increase in washing fastness conferred by increasing the number of anthraquinone molecules present in the dyestuff. Looseness to washing and particularly to kier boiling is often associated with dyestuffs which are easy to reduce completely to their leuco form such as flavanthrone and the acylaminoanthraquinones. As each anthraquinone radicle can be considered to act as an oxidising agent in such circumstances, then if several are present in the dyestuff molecule it should be more resistant to complete reduction and less dyestuff will be bled from the fibre during kier boiling. This is confirmed in practice.

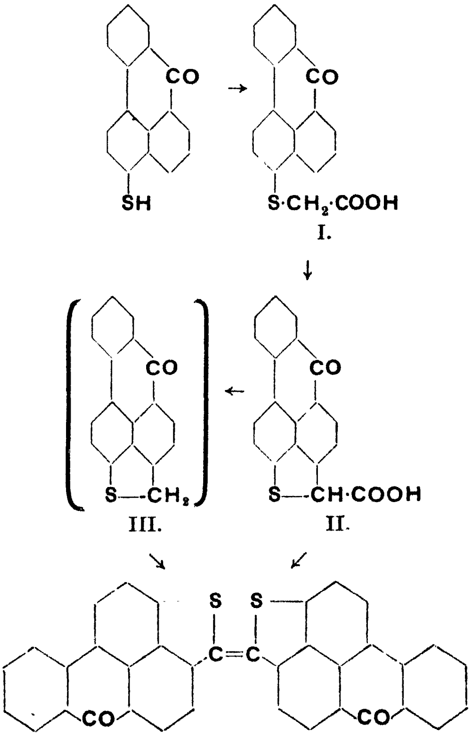
Excellent light fastness is also associated with the carbazole dyestuffs. They vary in shade between reddish-yellow and dark brown, and yield no pure primary colours. One anthraquinone carbazole derivative, prepared from carbazole itself, is of interest as a vat dyestuff, namely *Hydron Yellow G* 2 : 3, 6 : 7-diphthaloyl-*N*-ethylcarbazole, prepared by condensing phthalic anhydride with *N*-ethylcarbazole in presence of aluminium chloride, followed by ring-closure with sulphuric acid:



Hydron Yellow G (D.R.P. 261495).

Sulphurised Vat Colours.—There are a number of vat dyes obtained by processes involving sulphur or polysulphides the constitution of which is uncertain. They are mostly of inferior fastness.

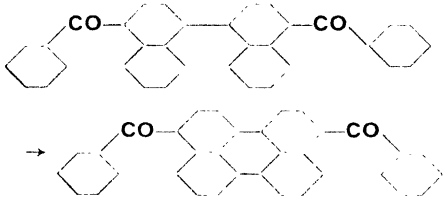
Indanthrene Olive G is produced by sulphur fusion of anthracene. It is of moderately good fastness, but not fast to bleach. *Cibanone Yellow R* is prepared by heating 2-chloromethylanthraquinone with sulphur followed by bleaching, and on the temperature being raised, *Cibanone Orange R* is produced. Neither of these products has very high fastness in any direction. *Cibanone Brown B* is similarly prepared from 1-amino-2-methylanthraquinone and *Cibanone Black B* from 2-methylanthraquinone by sulphur fusion at 300°–330°C. *Cibanone Blue 3G* is prepared from 4-methylbenzanthrone by sulphur fusion in a solvent such as naphthalene, or more readily from 3-chloro-4-methylbenzanthrone. Although this dyestuff is of about the same order of fastness as the other Cibanone colours, it is of special interest for printing, and is manufactured by the I.G. in a specially pure form as *Indanthrene Blue Green FFB*. The method of preparation confirms the constitution in a very elegant manner. Benzanthrone-3-thioglycollic acid (I), prepared from benzanthrone-3-mercaptan and chloracetic acid, is fused with caustic potash at 200°C. From the diluted alkaline solution a carboxylic acid (II) can be isolated by acidification, and this is converted to the dyestuff by heating in nitrobenzene; but the alkaline solution can be oxidised directly to the dyestuff by blowing in air at 70°C. The conversion probably passes through the intermediate stage (III) (B.P. 311047; G.P. 483154):

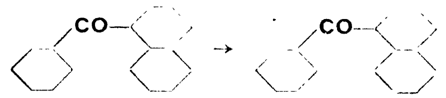


Indanthrene Blue Green FFB.

This dyestuff can be further converted by oxidation with nitric acid to *Cibanone Olive B*, or with mixed acid to *Cibanone Green B*. It seems probable that in such dyestuffs hydroxyl groups have been introduced (probably in the 2-positions).

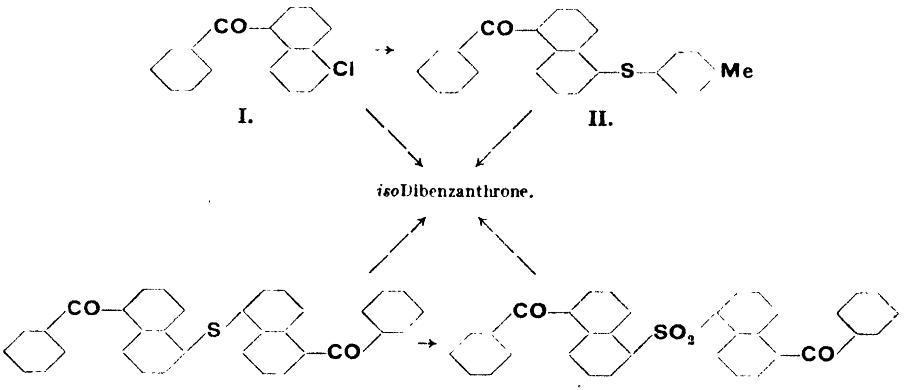
DIBENZANTHRONES.—The original colours of this class, mentioned in the introduction, were dibenzanthrone (*Violanthrene BS*) and its nitro- (*Viridanthrene B*) and dichloro- derivatives (*Violanthrene CD*), dibenzanthronquinoline (*Cyananthrene*) and *iso*dibenzanthrone (*Violanthrene R extra*) and its dichloro- (*Indanthrene Violet RR extra*) and dibromo- derivatives (*Indanthrene Violet B extra*). The constitution of dibenzanthrone has been proved by Scholl, who synthesised it from dibenzoyl-α-dinaphthyl by the use of the aluminium chloride fusion, known as Scholl's peri-synthesis (Scholl and Seer, Annalen, 1912, **394**, 111; 1913, **398**, 82), which had first given benzanthrone from phenyl-α-naphthylketone :





The dibenzanthrone and *iso*dibenzanthrone of the early manufacture were not pure, however, and considerable improvements in technique have been made in the intervening period, with an accompanying rise in tinctorial strength and purity of shade of the finished dyestuffs. The present range of the primary dyestuffs is as follows. Dibenzanthrone is represented by *Caledon Dark Blue 2R* and *BM*, the latter being bluer in shade than the former. Nitrodibenzanthrone is the basis of *Caledon Black NB*, *2BM*, and of *Caledon Green BP*, and similar British dyestuffs are the *Paradone* (H.) and *Anthrone* (Br.) *Blacks*. The Direct Blacks (*Caledon Direct Black AC*, *Indanthrene Direct Black RB*, *RR*, *G*) are prepared by treating nitrodibenzanthrone by heat, mild oxidation or other condensation so that they dye black irreversible to green by reduction. *Paradone Direct Black* is obtained by oxidation of dibenzanthrone with chromic acid and is probably hydroxylated.

In the case of *iso*dibenzanthrone, originally prepared by potash fusion of 3-chlorobenzanthrone, a greater technical advance has been made by its preparation *via* 3:3′-dibenzanthronyl sulphide or selenide, either of which yields *iso*dibenzanthrone in much higher yield and purity than hitherto. This improvement was originally traced through the 3-arylmercapto derivatives (II) of benzanthrone, which gave better yields than 3-chlorobenzanthrone (I), to the 3:3′-dibenzanthronyl sulphide or selenide (III) and sulphone (IV). The optimum temperature of fusion at the same time drops till with 3:3′-dibenzanthronyl sulphone only water-bath temperature is required.

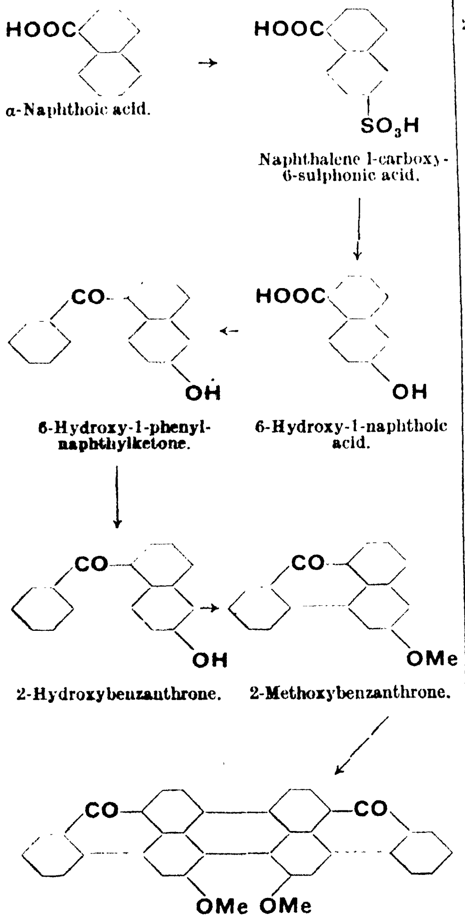


The increased yield and purity of *iso*dibenzanthrone is chiefly of interest as rendering possible the preparation of the two brilliant violets *Caledon Brilliant Purple 4R* and *Indanthrene Brilliant Violet 3B*, which are the dichloro- and dibromo- derivatives respectively. The shades are respectively redder and brighter, and bluer and brighter than the previous *2R* and *B* brands.

One defect common to all dibenzanthrone purples and violets is that of turning redder when moistened. No explanation of this phenomenon is yet available, but it is avoided in halogenated products prepared in special ways, *e.g.* by chlorination in solvents to at least a trichloro- derivative at temperatures up to 130°C. *Cibanone Blue RA* and *G*, and *Violet BW* and *Alizanthrene Navy Blue* are of this type.

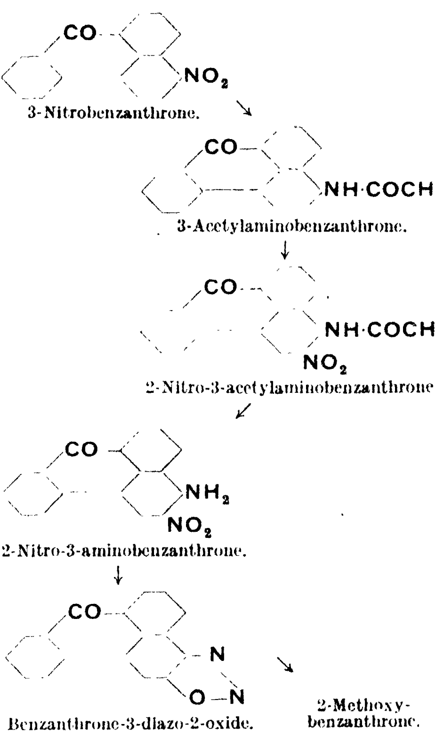
The most important vat dyestuff discovery since the Great War was a British one. *Caledon Jade Green X* (*Indanthrene Brilliant Green FFB*) (Davies, Fraser Thomson, and Thomas, B.P. 181304, 193431) consists of 2 : 2′-dimethoxydibenzanthrone, obtained by alkylation of 2 : 2′-dihydroxydibenzanthrone, and was discovered in 1920 (Fraser Thomson, J. Soc. Dyers and Col. 1926, **42**, 124 ; J.S.C.I. 1933, **52**, 946, 1935). Its constitution was established by Meister, Lucius and Brüning, who synthesised 2-methoxybenzanthrone from α-naphthoic acid (Synthesis I), and showed that this gave 2 : 2′-dimethoxydibenzanthrone on fusion with potash. While this route was not a feasible method of manufacture an alternative method proceeded from 3-nitrobenzanthrone through reduction, acetylation, nitration to the 2-nitro compound, deacetylation, diazotisation with formation of the diazo-oxide by loss of nitrous acid, and finally reduction to 2-hydroxybenzanthrone (Schirmacher, Zahn, Ochwat, and Wilke).

Synthesis I.



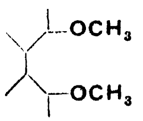
Caledon Jade Green X.

Alternative Synthesis.

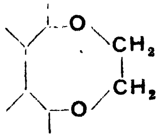

CO
NO₂
3-Nitrobenzanthrone.
CO
NH·COCH₃
3-Acetylaminobenzanthrone.
CO
NH·COCH₃
NO₂
2-Nitro-3-acetylaminobenzanthrone.
CO
NH₂
NO₂
2-Nitro-3-aminobenzanthrone.
CO
N
O—N
Benzanthrone-3-diazo-2-oxide.
2-Methoxy-benzanthrone.

2 : 2′-Dimethoxydibenzanthrone is, next to indanthrone, the most important anthraquinone dyestuff now manufactured (Kunz, *see* Literature, p. 429). It owes its success to several factors. Firstly it filled a gap as the first really brilliant fast vat green, being as bright as the basic greens (*e.g. Malachite Green cryst.*) and quite fast to bleaching. Secondly its dyeing behaviour is remarkably good, as it behaves well under the most varying conditions of temperature and alkalinity, and has a good affinity without a tendency to rush on to the fibre too quickly, which is rather marked in certain benzanthrone dyes. Lastly its fastness properties are exceedingly good all round.

Halogenation of 2 : 2′-dimethoxydibenzanthrone has to be carried out under conditions which do not allow dealkylation by the halogen acid formed. The dibromo- derivative is known as *Caledon Jade Green G* and the *2G* and *4G* brands are also halogenated derivatives. *Caledon Dark Blue G* is the ethylene ether of 2 : 2-dihydroxydibenzanthrone, and is greenish-blue in shade, though it differs by only two hydrogens from the dimethoxy compound.

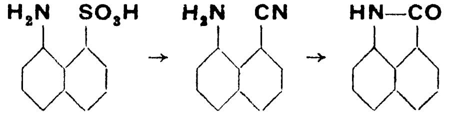


Jade Green.



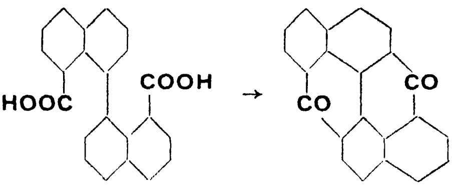
Dark Blue G.

Derivatives of other Homocyclic Quinones.—The recognition of the importance of 2 : 2′-dimethoxydibenzanthrone was immediate and led to great research activity and in particular a search was made for other vat dyes containing only carbon, hydrogen and oxygen. Just prior to the Great War Kalb discovered *anthanthrone*, which was obtained by the dehydration of 1 : 1′-dinaphthyl-2 : 2′- (or 8 : 8′-) dicarboxylic acid and Kalb showed that its dibromo- derivative was a bright orange (Ber. 1914, **47**, 1724). A technical method of synthesis was later found from naphthastyril. The latter can be prepared, *e.g.* from naphthalene peri-acid :



Peri-acid. Naphthastyril.

Naphthastyril when diazotised and treated with ammoniacal cuprous oxide gives good yields of 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid (I), from which anthanthrone (II) is readily formed by means of sulphuric acid. The product can be chlorinated (*Indanthrene Brilliant Orange GK*) or brominated (*Brilliant Orange RK*) and the products are chiefly prized on account of their brilliant shades (B.P. 260998; G.P. 280787).

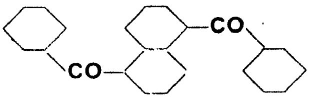


1 : 1′-Dinaphthyl-8 : 8′-dicarboxylic acid. Anthanthrone.

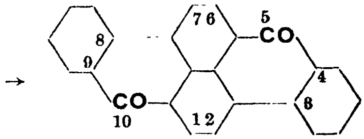
I. II.

Anthanthrone itself is of little value as a dyestuff owing to its pale colour and poor affinity. The halogenated derivatives, however, are very satisfactory in this respect.

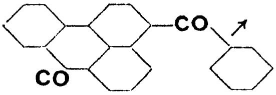
The *Dibenzopyrenequinones* were also discovered after the war by Meister, Lucius and Brüning. Benzanthrone when treated with benzoyl chloride and excess of aluminium chloride, first yields 3-benzoylbenzanthrone which undergoes ring-closure by dehydrogenation to benzoylenebenzanthrone or dibenzopyrenequinone. The latter reaction is materially assisted by oxidative methods, *e.g.* by passing air or oxygen, or halogens into the fluid melt, or by adding manganese dioxide. Dibenzopyrenequinone is marketed under the name of *Indanthrene Golden Yellow GK* (B.P. 205502, 220304). The inventors have also shown that this dibenzopyrenequinone can be prepared from 1 : 5-dibenzoylnaphthalene by dehydrogenation with aluminium chloride, while 1 : 4-dibenzoylnaphthalene yields an isomeric dibenzopyrenequinone of redder shade. These correspond to the more complicated *iso*dibenzanthrone and dibenzanthrone based on perylene instead of naphthalene :



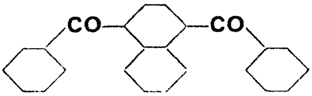
1 : 5-Dibenzoylnaphthalene.



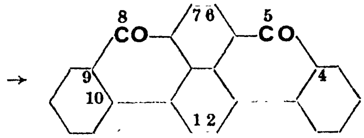
*iso*Dibenzopyrenequinone (3 : 4, 8 : 9 dibenzopyrene-5 : 10-quinone). (Indanthrene Golden Yellow GK.)



3-Benzoylbenzanthrone.

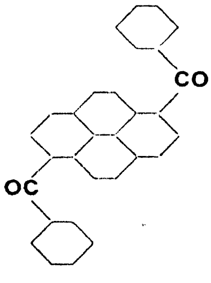


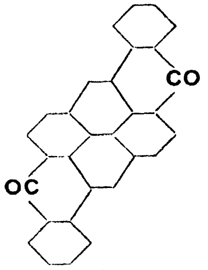
1 : 4-Dibenzoylnaphthalene.



Dibenzopyrenequinone (3 : 4, 9 : 10-dibenzopyrene-3 : 8-quinone).

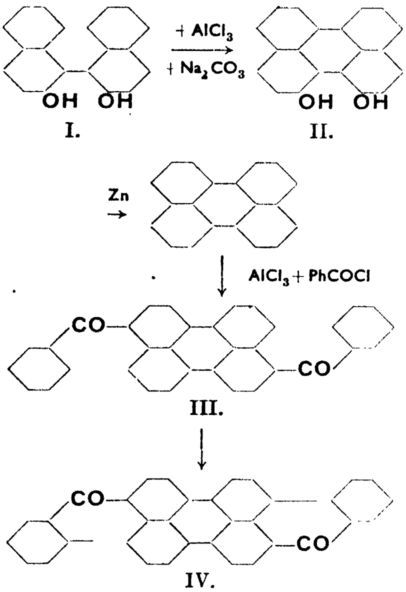
It may be noted here that Scholl had shown earlier that pyranthrone could be synthesised by the same type of method from 3 : 8-dibenzoylpyrene (Ber. 1910, **43**, 513).





Pyranthrone.

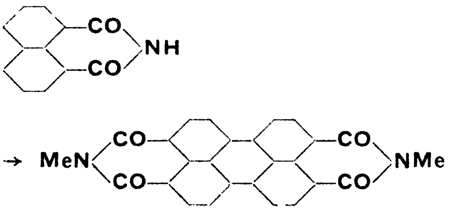
Perylene.—The success of Scholl's method in other fields led to increased interest in perylene, which was first synthesised by him in small yield from 1 : 1′-dinaphthyl. It is now fairly easily obtainable from β-dinaphthol, prepared by ferric chloride oxidation of β-naphthol. The Hansgirg method for the production of perylene involves heating β-dinaphthol (I) to 500° with phosphorus trichloride. The Zincke-Pereira method, which is claimed to be an improvement, uses β-dinaphthol, aluminium chloride and an alkaline substance, such as soda, at a comparatively low temperature (150°–170°). The product is 1 : 12-dihydroxy perylene (II) (B.P. 165771, 191363). This is converted into perylene by distillation with zinc dust and a hygroscopic substance (B.P. 165770, 199401). Finally perylene is dibenzoylated and the product (III) baked with aluminium chloride at 150°–170°. The product is *iso*dibenzanthrone (IV) (B.P. 212252).



I. II. III. IV.

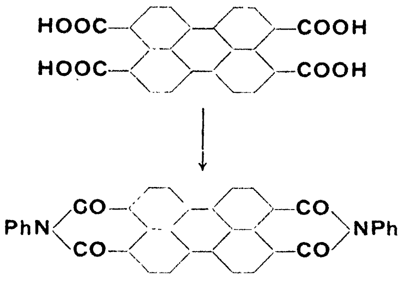
(*Cf.* Zincke and co-workers, Ber. 1925, **58** [B], 323, 799, 2222 ; Scholl and Seer, Annalen, 1912, **394**, 126 ; Marschalk, Bull. Soc. chim. 1927 [iv], **41**, 707).

Other vat dyes based on perylene are those derived from naphthalimide. The latter on potash fusion yields dinaphthalimide (*Caledon Claret R*), which on alkylation yields *Caledon Red GG* (dimethyldinaphthalimide) (B.P. 26690, 1913).



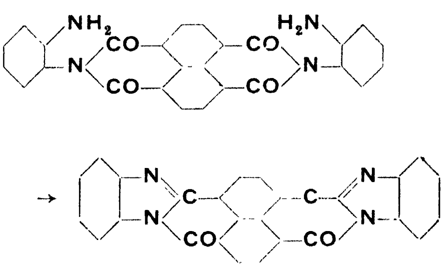
Dimethyldinaphthalimide.

When dinaphthalimide is treated with strong sulphuric acid, perylene tetracarboxylic acid is produced and the latter readily gives arylamides by condensation with arylamines, and these are bright red vat dyes (V).



V.

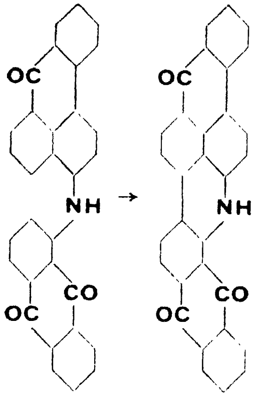
A recent development of more interest is the series of dyes derived from naphthalenetetracarboxylic acid. When this acid is condensed with o-aryldiamines, the di-imides first formed readily part with two further molecules of water and yield iminazoles (B.P. 313887, 369604).



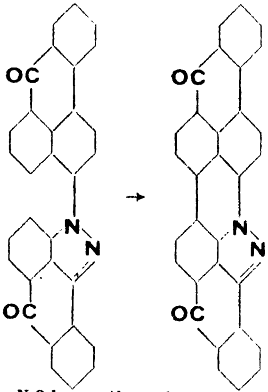
Naphthoylene dibenziminazole.

The dyestuff *Indanthrene Scarlet 2G* is of this type. It will readily be seen that theory demands that two isomers of the di-iminazole type, *cis-* and *trans-* should exist and in due course methods were obtained for separating the mixture (*Indanthrene Scarlet 2G*) into its components. The main component was found to be a brilliant orange (*Indanthrene Brilliant Orange GR*) associated with a bluish red of less interest. *Indanthrene Brilliant Orange GR* is a colour of very good properties and exceptionally bright shade (B.P. 366705, 391259).

Recent Research.—The chemistry of new polycyclic systems continues to be studied, and it is worthy of note that increasing use is being made of pyridine or pyrrole to replace benzene rings in complicated systems. Examples are the compounds obtained by condensing 3-halogenobenzanthrone with aminoanthraquinones or pyrazolanthrone, followed by further ring-closure by means of fused alkali or other means. In the latter case a compound resembling dibenzanthrone is obtained, but the shade is noticeably changed towards blue. The intermediate dyes blue-green shades.

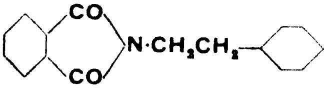


3 : 1′-Anthraquinonyl-iminobenzanthrone.

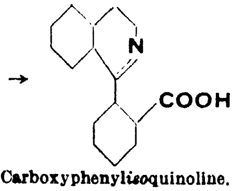


N-3-benzanthronyl pyrazolanthrone.

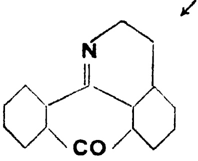
Benzanthrones with one benzene ring substituted by a pyridine ring have been tentatively named *azabenzanthrones*. These may be obtained in several ways. Thus β-phenylethylphthalimide, treated with aluminium chloride and then with sulphuric acid, undergoes changes which may be represented as follows :



β-phenylethylphthalimide.

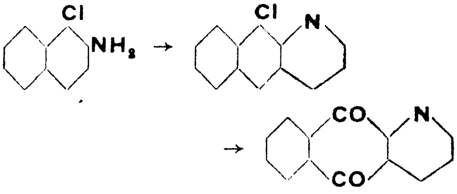


1-*o*-Carboxyphenyl*iso*quinoline.



1-Azabenzanthrone.

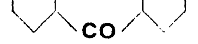
Azanthraquinone is obtained by commencing with 1-chloro-2-naphthylamine, carrying out a Skraup reaction, and oxidising :



Azanthraquinone.

This again can yield azabenzanthrones by condensation with a three-carbon chain (I.G., B.P. 427485).

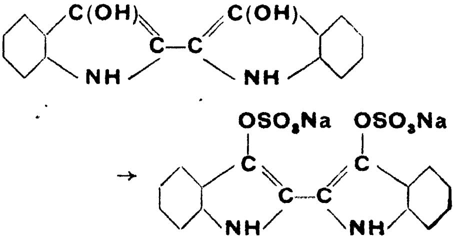
2-*Azabenzanthrones* are prepared by heating carboxymethyl amides of anthraquinone-1-carboxylic acid to high temperatures. Thus anthraquinone-1-carboxyethylglycocollate is saponified and at 275° yields 3-hydroxy-2-azabenzanthrone and the 1-carboxylic acid thereof, which group can be removed with alkali to give 3-hydroxy-2-azabenzanthrone:



3-Hydroxy-2-azabenzanthrone (1-carboxylic acid).

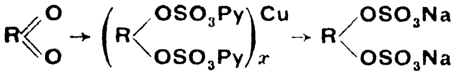
SOLUBILISED VAT DYES.—The vat dyes are applied by means of a caustic alkaline hyposulphite vat and on this account cannot be easily applied to wool and silk, which are not resistant to caustic alkali. In addition, for many purposes the reducing bath is cumbersome and expensive. It had, therefore, long been a problem to achieve the vat colour fastness on the fibre by a simpler method of application.

Bader and Sunder in 1924 discovered a method of solubilising indigo by esterifying leuco indigo with oleum or chlorosulphonic acid in dimethylaniline solution, the product being isolated as the sodium salt by alkaline distillation and evaporation :



Indigosol O.

This method is not so convenient for the anthraquinone vat dyes, as the leuco compounds in the latter case are not so readily isolated in a pure form, but Scottish Dyes discovered that the vat dyestuffs reacted readily with sulphuric anhydride in solution in a tertiary base in presence of a metal such as copper or zinc. A metal-pyridine complex (I) containing the pyridine salt of the ester of the leuco vat dyestuff is formed directly and from this the sodium salt (II) is prepared by decomposing the complex with alkali, removing the tertiary base by distillation and the copper oxide by filtration and salting out or evaporating the liquid.

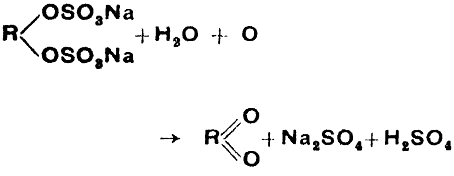


$$\mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}} \rightarrow \left(\mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{OSO_3Py}}{\mathrm{OSO_3Py}}\right)_x\mathrm{Cu} \rightarrow \mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{OSO_3Na}}{\mathrm{OSO_3Na}}$$

I. II.

The fact that I is formed under strictly anhydrous conditions shows that II is formed directly without passing through the leuco compound $\mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}$ as in the Bader and Sunder method, as no source of hydrogen is available under the conditions of the reaction.

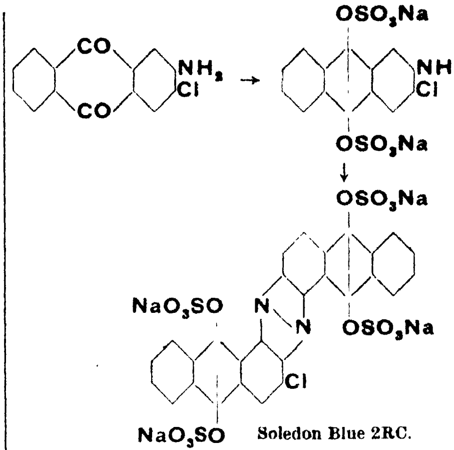
In this way a wide range of *Soledon Colours* has been prepared from the parent vat dyestuffs, including *Soledon Jade Green, Purple 2R, Yellow G, Brilliant Orange 4R, Dark Blue B, 2R*, etc. These soluble esters are characterised by stability in the alkaline state, but in presence of acid oxidising agents they regenerate the parent vat dyestuff.



$$\mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{OSO_3Na}}{\mathrm{OSO_3Na}} + \mathrm{H_2O} + \mathrm{O} \rightarrow \mathrm{R}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}} + \mathrm{Na_2SO_4} + \mathrm{H_2SO_4}$$

Thus cotton, wool or silk (natural or artificial) steeped in the solution of the alkali salt, when squeezed and treated with an acid oxidising agent such as sodium nitrite and hydrochloric acid, acquires the shade of the parent dyestuff.

Anthraquinone itself and many of its intermediates can be converted into the esters of their leuco compounds and where the necessary further reactions can be carried out in alkaline solution dyes can thus be prepared. An example is the synthesis of *Soledon Blues R, 2RC*. These are prepared by esterifying 2-amino- and 3-chloro-2-aminoanthraquinone respectively and then oxidising the esters in alkaline solution. The products are thus the tetrasulphuric esters of the corresponding dyestuffs :



Soledon Blue 2RC.

Brilliancy of Shade.—It is worth recording here that the anthraquinone colours were formerly considered to be dull in shade. As a result of technical advances in manufacture, however, the following comparisons of the brightest vat colours with basic triphenylmethane colours are made :

1. *Indanthrene Yellow 5GK* equal to Auramine O.
2. *Indanthrene Brilliant Orange GR* equal to Flavophosphine R.
3. *Caledon Brilliant Blue 3G* equal to Methylene Blue.
4. *Caledon Brilliant Purple 4R* equal to Crystal Violet O.
5. *Caledon Jade Green X* equal to Malachite Green cryst.

Literature.—For further information the following references are collected together. The fundamental source of information is the voluminous mass of patent literature of Britain, Germany, France, Switzerland and the United States of America. Digests of this are available chiefly in Friedländer, "Fortschritte für Teerfarbenchemie," Vols. 1–20 (1870–1933) Several useful text-books are : Barry Barnett, "Anthracene and Anthraquinone," London, Baillière, Tindall, and Cox, 1921 ; Thorpe and Ingold, "Vat Dyes," London, Longmans, 1923 ; Thorpe and Linstead, "Synthetic Dyestuffs," London, C. Griffin, 1933 ; Houben, "Das Anthracen und die Anthrachinone," Leipzig, Thieme, 1929 ; and Fierz-David, "Kunstliche Organische Chemie," Berlin, Springer, 1926. A useful historical summary is given by Kränzlein, "Kunstliche Organische Farbstoff," Enke, Stuttgart, 1935, and some recent research developments are summarised by Kunz, Bull. Soc. Ind. Mulhouse, 1934, 3. Other summaries of value are those of Mason, Industrial Chemist, 1929, 111, 137, Corbellini and Aymar, Giorn. Chim. Ind. Appl. 1928, **10**, 196, and Lukin, Anilinokras. Prom. 1934, **4**, 536. Annual Reports of the Progress of Applied Chemistry (Anthraquinone Dyestuffs Section) give detailed précis of patent literature.

Reference works of much value are the "Colour Index" of the Society of Dyers and Colourists (Rowe) and "Farbstoff Tabellen" (Schultz, Leipzig, Akad.-Verlag G.m.b.H., 1931).

LIST OF ABBREVIATIONS.

B. Badische Anilin und Soda Fabrik.
By. F. Bayer & Co.
M.L.B. Meister, Lucius and Brüning.

These firms subsequently amalgamated as:

I.G. Interessen Gemeinschaft Farbenindustrie Akt. (*Indanthrene Alizarin*).
Br. Brotherton & Co. (*Anthrone*).
H. L. B. Holliday & Co. (*Paradone*).
I.C.I. Imperial Chemical Industries (*Caledon, Solway, Soledon, Alizanthrene*).
S.C.I.B. Society of Chemical Industry, Basle (*Cibanone*).
W. R. Wedekind & Co. (*Erweco*).

R. F. T.

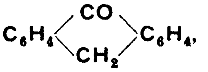
ANTHRAQUINONE Blue SR, Green GX, Violet *v.* ANTHRAQUINONE DYESTUFFS.

ANTHRA RUBINE *v.* ANTHRAQUINONE DYESTUFFS.

ANTHRARUFIN *v.* ALIZARIN AND ALLIED DYESTUFFS.

ANTHRIMIDES *v.* ANTHRAQUINONE DYESTUFFS.

ANTHRONE, ANTHRANOL, AND ALLIED COMPOUNDS. Anthrone,

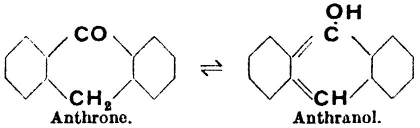


$$C_6H_4\left\langle\begin{matrix}CO\\CH_2\end{matrix}\right\rangle C_6H_4,$$

is obtained by the reduction of anthraquinone by the following methods: (I) A boiling glacial acetic acid solution of anthraquinone is treated with hydrochloric acid and powdered tin or iron and when the reaction is over the anthrone is precipitated from the filtered product by the addition of water. (II) A solution of anthraquinone in concentrated sulphuric acid is reduced at a temperature of 30°–40° with aluminium powder and filtered through porous glass; on diluting the filtrate with water the anthrone is obtained in almost theoretical yield. (III) Anthraquinone is hydrogenated under pressure in various solvents at a temperature of 160°–170° in the presence of finely divided nickel; by careful control of the conditions theoretical yields of anthrone can be obtained. (IV) Anthraquinone is heated under pressure with aqueous caustic soda and glucose at 200°–230°; on the technical scale *molasses* is substituted for the glucose. (V) Reduction of anthraquinone with sodium hyposulphite under the usual conditions gives rise to anthraquinol, but by the prolonged action of this reagent anthrone can be obtained in 75% yield.

Anthrone crystallises from acetic acid in colourless needles the melting-point of which given in the literature varies between 150° and 170°. It is insoluble in cold aqueous alkali hydroxides, but on boiling with these reagents it enolises and slowly passes into solution as the alkali derivative of anthranol. When this latter solution is cooled and acidified with cold mineral acid anthranol is thrown down as a golden-brown precipitate.

Anthrone and anthranol form a typical pair of desmotropes, *i.e.* they are isomeric compounds each of which can be obtained pure in the solid state but when either enters solution trans-annular migration of hydrogen takes place until a definite equilibrium between the two tautomerides is established. The actual position of the equilibrium and the time taken for it to be established depend upon the nature of the solvent, but in all cases the equilibrium lies well over on the ketonic side, *i.e.* anthrone is the more stable of the two desmotropes.



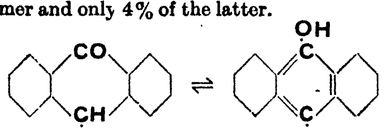
Anthrone. Anthranol.

Tautomeric change also takes place at the fusion temperature and if molten anthrone is rapidly chilled the equilibrium is fixed in this position and consequently the product is partly soluble in cold aqueous caustic alkalis. When anthrone is heated with aqueous caustic soda the anthranol is removed as fast as it is formed from the equilibrium mixture as the soluble sodio derivative and consequently enolisation proceeds until the whole of the anthrone has been converted into anthranol.

The chief differences between the two tautomerides is shown in the following table.

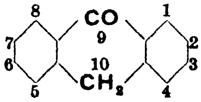
Anthrone.	*Anthranol.*
Insoluble in cold aqueous alkali hydroxides.	Easily soluble in cold aqueous alkali hydroxides.
Colourless.	Golden brown.
Non-fluorescent.	Strongly fluorescent (blue).
Does not couple with diazonium salts.	Couples easily with diazonium salts.
Reacts slowly with nitrosodimethylaniline.	Reacts quickly with nitrosodimethylaniline.
Not affected by bromine, iodine, ferric chloride, or amyl nitrite when dissolved in slowly enolising solvents.	Rapidly oxidised by bromine, iodine, ferric chloride or amyl nitrite to dihydrodianthrone, which is non-fluorescent.

The last of these differences has been made use of by Kurt Meyer to determine the equilibrium position under various conditions. The mixture is titrated with bromine solution until the fluorescence, viewed in an intense beam of light, has completely disappeared. In 0·1% alcoholic solution the equilibrium solution contains 89% anthrone and 11% anthranol. The presence of hydroxyl groups in either of the outer rings shifts the equilibrium still further over on to the ketonic side, but the presence of a hydroxyl group in the *meso* position exerts a powerful stabilising influence upon the enolic form. Thus the equilibrium mixture of anthraquinol and oxanthrone (*meso*-hydroxyanthrone) contains 96% of the former and only 4% of the latter.



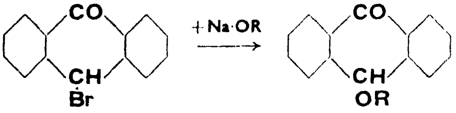
Oxanthrone. Anthraquinol.

Reactions of Anthrone.—For purposes of reference the positions in the anthrone nucleus are numbered as shown in the accompanying scheme ; the 10-position is usually referred to as the *meso*-position. Anthrone reacts with hydroxylamine and with phenylhydrazine to form an oxime and a phenyl-hydrazone respectively. On nitration it yields *meso*-nitroanthrone, m.p. 137°, in good yield. Bromine reacts readily with anthrone in carbon disulphide or chloroform solution to give first *meso*-bromoanthrone, m.p. 148°–151°, and finally *meso*-dibromoanthrone, m.p. 157°. With chlorine the reaction is so vigorous that *meso*-dichloroanthrone, m.p. 132°–133°, is the only product which can be isolated with ease ; this compound can also be obtained by the chlorination of tolyl phenyl ketone.

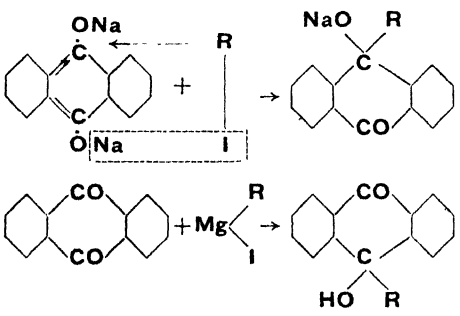


Hydrolysis of *meso*-dibromoanthrone with boiling aqueous acetone gives rise to *meso*-hydroxyanthrone or oxanthrone ; this substance, however, is more easily obtained by the direct oxidation of anthracene in aqueous acetone solution with bromine. Oxanthrone is insoluble in cold aqueous alkali hydroxides, but on boiling with these reagents it enolises and passes into solution as the intense red di-alkali derivative of anthraquinol. Acidification of this solution in the cold causes precipitation of anthraquinol the more stable of the two desmotropes.

Treatment of *meso*-bromoanthrone with alkali alkoxides gives rise to O-alkyl derivatives or ethers of oxanthrone.



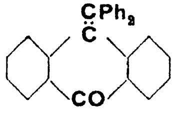
The C-alkyl derivatives of oxanthrone are obtained by the *direct alkylation of anthraquinol* with alkali and alkyl iodides, and also by the action of Grignard compounds upon anthraquinone provided the latter is present in excess, in order to avoid the attack of the second keto group by the Grignard reagent.



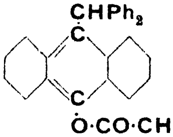
The *meso*-hydroxyl group in C-alkyloxanthrones is easily replaced by chlorine by the reaction of phosphorus pentachloride to give *meso*-alkylchloroanthrones. In the case of *meso*-phenyloxanthrone the activity of the hydroxyl group is so great that the action of gaseous hydrogen chloride and hydrogen bromide on the compound, in benzene or chloroform solution, yields *meso*-phenylchloro- and phenylbromoanthrone respectively.

meso-Phenylchloroanthrone condenses with benzene in presence of aluminium chloride to give *meso*-diphenylanthrone. The latter may also be obtained by the action of sulphuric acid on a mixture of *meso*-phenyloxanthrone and benzene or by treatment of *meso*-dichloroanthrone with benzene and aluminium chloride.

The methylene group in anthrone readily undergoes condensation with ketones: thus, with benzophenone, anthrafuchsone is formed which on treatment with zinc dust in acetic acid solution is reduced at the double bond; enolisation and acetylation then occur, with subsequent formation of 10-diphenylmethylanthranol-9-acetate.



Anthrafuchsone.



10-Diphenylmethyl anthranol-9 acetate.

Anthrone condenses with isatin to give indolanthracenelignône.

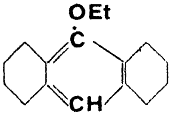
Anthrone is reduced by tin and hydrochloric acid only with difficulty, but with zinc and hydrochloric acid it is readily reduced to a mixture of dianthranyl and anthrapinacone (*v. infra*).

Anthrone condenses with glycerol in the presence of sulphuric acid to yield benzanthrone which is important in industry.

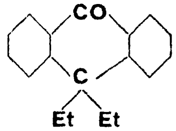
Reactions of Anthranol.—Anthranol crystallises in golden brown needles which sinter at 120° and melt to a clear liquid at 152°. Even in the solid state it slowly passes into anthrone the conversion being very gradual at ordinary temperatures but rapid as the melting-point is approached. Its solutions in organic solvents possess an intense blue fluorescence. It is easily soluble in cold aqueous caustic alkalis with production of a deep yellow solution.

Alkylation of anthranol with ethyl iodide and caustic soda gives rise to three products, viz. :

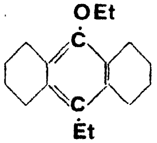
I. The normal O-ethyl ether.
II. *meso*-Diethylanthrone.
III. *meso*-Ethylanthranol ethyl ether.



I.



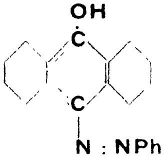
II.



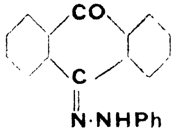
III.

Alkylation with alkyl sulphates and with alkyl *p*-toluene sulphonates, however, yields only the normal **O**-ethers of anthranol.

The **O**-ethers of anthranol couple readily with diazonium salts but the compound is quantitatively dealkylated during the process: thus benzene diazonium chloride and **O**-alkylanthranols yield *meso*-benzeneazoanthranol. This latter compound is tautomeric with anthraquinone monophenylhydrazone.

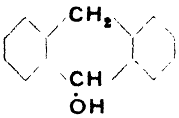


Benzeneazoanthranol.

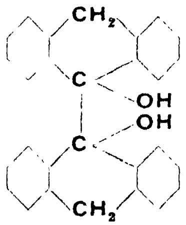


Anthraquinone phenylhydrazone.

Dihydroanthranol.—Dihydroanthranol is obtained together with anthrapinacone by the reduction of anthraquinone with zinc dust and ammonia.



Dihydroanthranol.

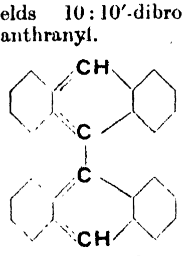


Anthrapinacone.

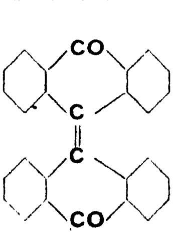
Dihydroanthranol is an unstable, colourless compound, m.p. 76°, which on boiling in aqueous suspension is rapidly converted into anthracene by the loss of the elements of water. It reacts readily with bromine giving anthracene and finally *meso*-dibromoanthracene. *meso*-Alkyldihydroanthranols are obtained by the reaction of Grignard compounds on anthrone: these resemble the parent compound inasmuch as they readily split off water with the production of *meso*-alkylanthracenes.

DIANTHRANYL : DIANTHRANOL : DIHYDRODIANTHRONE AND DIANTHRONE.

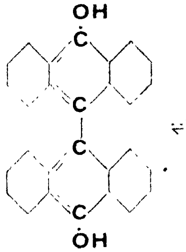
Anthrapinacone on boiling with water loses two molecules of water with formation of dianthranyl, which can also be obtained by the reduction of anthraquinone in acetic acid solution with tin and hydrochloric acid under carefully controlled conditions. With bromine and nitric acid respectively dianthranyl yields 10 : 10′-dibromo- and 10 : 10′-dinitrodianthranyl.



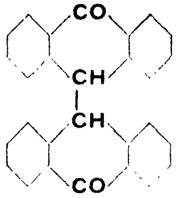
Dianthranyl.



Dianthrone.



Dianthranol.

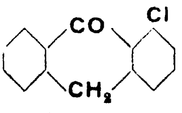


Dihydrodianthrone.

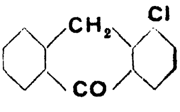
By the reduction of anthraquinone with zinc dust and aqueous caustic soda under pressure at 160°, 10 : 10′-dihydroxydianthranyl, or dianthranol, is obtained. Dihydrodianthrone, the ketonic desmotrope of dianthranol, is best obtained by Dimroth's method of oxidising anthranol with ferric chloride in boiling glacial acetic acid solution. While anthrone enolises and dissolves easily when heated with aqueous caustic alkali, dihydrodianthrone enolises and dissolves only when heated under pressure at temperatures above 100° with aqueous alkali hydroxides. It passes readily, however, into the soluble dipotassio-derivative of dianthranol when heated with alcoholic potash and on acidification of this solution dianthranol is precipitated. Dianthranol is a more stable compound than anthranol and it must be boiled in alcoholic solution with hydrogen chloride in order to convert it into its tautomeride, dihydrodianthrone. By the action of mild oxidising agents, such as potassium persulphate, dianthranol is converted into dianthrone. Dihydrodianthrone however, is unaffected by fuming nitric acid.

Treatment of *meso*-monobromoanthrone with ammonia causes elimination of one molecule of hydrogen bromide from two molecules of the bromoanthrone, with formation of 9-bromodihydrodianthrone. When the latter, or the parent bromoanthrone itself, is refluxed in xylene solution with copper bronze another molecule of hydrogen bromide is removed with production of dianthrone. Dianthrone is a very stable compound, converted by the action of strong reducing agents first into dianthranol, and finally into dihydroanthracene. With powerful oxidising agents it yields anthraquinone.

Derivatives of Anthrone.—Substituted derivatives of anthrones are usually obtained by the reduction of the corresponding anthraquinone by the methods outlined above. The orientation of the product depends upon which keto group in the anthraquinone molecule undergoes reduction and not infrequently two isomeric compounds are simultaneously produced: thus α-chloroanthraquinone yields a mixture of 1-chloroanthrone (9) and 1-chloroanthrone (10) [*i.e.* 4-chloroanthrone (9)].



1-Chloroanthrone (9).



1-Chloroanthrone (10).

1-Hydroxyanthrone (10), 1:2-dihydroxyanthrone (10) [*anthrarobin*], 1:8-dihydroxyanthrone (9) [*cignolin*], and 1:8-dihydroxy-3-methylanthrone (9) [*chrysophanic acid*] find application in the chemotherapy of skin diseases.

1:2:3- and 1:2:6-trihydroxyanthrone (9) and also 1:2:7-trihydroxyanthrone (10) have been obtained by the reduction of anthragallol, flavopurpurin and anthrapurpurin respectively.

Derivatives of anthrone can often be prepared by nuclear synthesis. Condensation of phthalic anhydride or substituted phthalic anhydrides with benzene or benzene derivatives gives rise to substituted benzoylbenzoic acids, which by reduction with zinc dust and caustic soda are converted into the corresponding benzylbenzoic acids. Treatment of the latter with dehydrating agents such as sulphuric acid effects closure of the ring with loss of water and formation of the substituted anthrone. In many cases, however, simultaneous oxidation occurs during the last reaction and the product obtained is the substituted anthraquinone; for example, benzylbenzoic acid itself yields anthraquinone and no trace of anthrone (*see* art. ANTHRAQUINONE, under " Nuclear Syntheses ").

(For a comprehensive account of Anthrone, Anthranol, and allied ring systems, and for full references to the literature, *see* Houben, " Das Anthracen und die Anthrachinone," G. Thieme, Leipzig, 1929.) A. A. G.

ANTHROPHYLLITE *v.* ASBESTOS.

ANTIARIN. The Java arrow poison from *Antiaris toxicara*; consists of two isomeric glycosides which are hydrolysed to a genin of unknown constitution, rhamnose, and a methyl pentose of unknown structure provisionally termed antiarose (Kiliani, Ber. 1913, **46**, 667, 4029). E. F. A.

ANTI-CHLOR. An anti-chlor is a reagent formerly used to remove from materials bleached with hypochlorite the last traces of free chlorine, which would otherwise cause rotting. The best-known anti-chlor is sodium thiosulphate, but sodium hyposulphite and sulphurous acid are also used. Other substances recommended as anti-chlors are hydrogen peroxide, calcium sulphide, stannous chloride, ammonia and sodium nitrite. Improved methods of working have now rendered this process unnecessary.

ANTICOL. Trade name for a preparation of colloidal antimony. Parasiticide.

ANTICORODAL *v.* ALLOYS, LIGHT.

ANTI-FEBRIN. A trade name for acetanilide, **PhNH·COMe**, formerly used as an antipyretic.

ANTIDIN. Phenyl ether of glycerol.

ANTIFORMIN. A trade name for a solution of sodium hypochlorite and sodium hydroxide, used as a disinfectant.

ANTIFUNGIN. Magnesium borate employed as a fungicide,

$$\mathrm{Mg(BO_2)_2 2Mg(OH)_2,7H_2O}.$$

Antiseptic.

ANTIHYPO. A solution of potassium percarbonate used for destroying sodium thiosulphate (*hypo*) in photographic negatives and prints.

ANTILEPROL. Trade name for a preparation consisting of the ethyl esters of the fatty acids of chaulmoogra oil.

ANTILEUTIN. Trade name for potassium ammonium antimonyl tartrate. Trypanosomicide.

ANTIMONIALS, ORGANIC. The organic chemistry of antimony was initiated with the synthesis in 1850 of triethylstibine by Löwig and Schweitzer (Mitth. d. Zürch. Naturforsch. Gesellschaft, 1850, **45**, 1; Annalen, 1850, **75**, 315, 327).

This synthesis was immediately extended by H. Landolt (Annalen, 1851, **78**, 91) and further investigations of aliphatic antimonials were made by Hofmann (1857) and by Buckton (1860).

Aromatic antimonials were not prepared until thirty years later, when Michaelis and his collaborators developed a general method for the synthesis of antimony compounds containing one, two and three aryl groups.

In 1910 these researches were revised by Morgan and Micklethwait (J.C.S. 1911, **99**, 2293), who showed that triphenylstibine on heating with antimony chloride yields both mono- and diphenylstibine chlorides, and who determined the effect of the antimony complex on the orientation of a nitro- group. Similar investigations were made independently by P. May, who also studied the reduction of the nitrated arylantimony compounds (J.C.S. 1912, **101**, 1033).

The considerable increase in our knowledge of aromatic antimonials during recent years, arising from their important therapeutic value in certain tropical diseases, has been made possible largely by the development of the diazo synthesis of these products. First employed by the Chemische Fabrik von Heyden of Dresden in 1911 (G.P. 254421), it has more recently been thoroughly studied by H. Schmidt and others.

Due largely to the greater experimental difficulties contingent on the feebler affinity of antimony for hydrocarbon radicals, syntheses of aliphatic antimonials are few compared with those in the arsenic series. Indeed, while the organic chemistry of arsenic began with cacodyl, in the case of antimony no primary or secondary antimonials, with the exception of ethyldiiodostibine, were known until 1926, when Morgan and Davies (Proc. Roy. Soc. 1926, **110**, A, 523) completed the series of methylstibine derivatives; although detected, the antimony analogue of cacodyl was not actually isolated, but more recently Paneth and Loleit (J.C.S. 1935, 366) have succeeded in obtaining both this compound and its ethyl homologue.

Antimony can also form a member of a heterocyclic system: the antimony analogues of carbazole and dihydrostibacridine have been obtained by Morgan and Davies, while Steinkopf, Schubart, and Roch have prepared antimony *cyclo*pentamethylene chloride.

SYNTHESIS OF ALIPHATIC ANTIMONIALS.

(1) Interaction of an alkyl halide with antimony or an alloy of antimony.—Methyl iodide heated with antimony in a sealed tube at 140° yields *trimethylstibine diiodide*,

$$Sb(CH_3)_3I_2,$$

(Buckton, J.C.S. 1860, **13**, 120), whereas when it reacts with an alloy of sodium and antimony at ordinary temperature there is obtained trimethylstibine and tetramethylstibonium iodide (Landolt, *l.c.*).

(II) Interaction of a metallic alkyl with an antimony halide.—Zinc or mercury diethyl reacts with antimony trichloride to give triethylstibine (Hofmann, Annalen, 1857, **103**, 357 ; Buckton, J.C.S. 1863, **16**, 22).

At present the Grignard reaction is almost exclusively employed in the preparation of aliphatic antimonials and yields of 60–70% of trimethylstibine may be obtained by interaction between antimony trichloride and methyl magnesium iodide (Hibbert, Ber. 1906, **39**, 160 ; Dyke, Davies, and Jones, J.C.S. 1930, 463).

(III) Interaction of sodium with a mixture of alkyl and antimony halides.—The Fittig reaction, hitherto used in the preparation of aryl derivatives of antimony, has now been extended to the manufacture of alkyl antimonials. A mixture of the alkyl and antimony halides in toluene is carefully added to sodium under warm toluene and the mixture refluxed.* Mixed aryl-alkyl stibines may be prepared by using arylstibine halides in place of the inorganic antimony salt (B.P. 303092).

ALIPHATIC ANTIMONIALS.

Trimethylstibine, $SbMe_3$.—Originally synthesised by method I above, it is most conveniently prepared through the Grignard reaction.

Colourless liquid, b.p. 80·6°, d^{15} 1·523, odour of onions. Soluble in ether, slightly soluble in water or alcohol ; spontaneously inflammable in air or chlorine. Its alcoholic solution forms with platinous chloride two isomeric additive compounds, a soluble yellow monomeride, *bistrimethylstibinedichloroplatinum* $[2Me_3Sb,PtCl_2]$, and an orange insoluble dimeride, *tetrakistrimethylstibine platinous platinochloride*,

$$[Pt,4Me_3Sb]PtCl_4.$$

The latter substance passes into the former at 60° or on keeping for some months at ordinary temperature.

Similar compounds are obtained with palladous chloride but are much less stable (Morgan and Yarsley, J.C.S. 1925, 184).

The *dihalides*, Me_3SbX_2, produced by direct addition of the halogens, are colourless crystalline substances slightly soluble in warm water. The diiodide when heated with iodine gives a *hexaiodide*, Me_3SbI_6, as dark green needles, m.p. 68°–70° (Lowry and Simons, Ber. 1930, **63**, 1598). These authors have also studied the molecular conductivities of the halides and oxyhalides.

Treatment of the dihalides with silver nitrate or sulphate gives rise to a *nitrate* or *sulphate* respectively ; the latter substance reacts with barium hydroxide to form *trimethylstibine oxide*, which may also be produced by regulated oxidation of trimethylstibine. Energetic oxidation, especially of the higher aliphatic stibines, causes the formation of complexes of the type $R_3SbO\cdot Sb_2O_3$, described as stibinic metantimonites (Dyke and Jones, J.C.S. 1930, 463, 1921).

A *trimethylstibine sulphide*, Me_3SbS, is also known.

Tetramethylstibonium iodide, $Me_4SbI\cdot 1\frac{1}{2}H_2O$.—Formed by direct union of trimethylstibine and methyl iodide. Hexagonal plates, very soluble in water or alcohol, less so in ether ; bitter saline taste.

Tetramethylstibonium hydroxide.—Deliquescent crystalline mass obtained by treating the iodide with moist silver oxide; it is a strong base and resembles caustic potash ; its salts are crystalline and devoid of emetic action. The *chloride* forms an orange-yellow *platinichloride* only slightly soluble in water.

Similar series of products are obtained from *triethylstibine*, b.p. 158·5/730 mm., d^{16} 1·3244 ; *tri*-n-*propylstibine*, b.p. 100°/25 mm., d^{25} 1·241 ; *tri*-n-*butylstibine*, b.p. 131°/12 mm., d^{25} 1·323 ; *tri*-n-*amylstibine*, b.p. 168°/16 mm., d^{25} 1·136 ; *tri*-iso-*amylstibine*, b.p. 149°/14 mm., d^{25} 1·227 ; *tri*-n-*hexylstibine*, b.p. 190°/10 mm. (decomp.) (Löwig and Schweitzer, Annalen, *l.c.*; Hofmann, *l.c.* ; Dyke and Jones, *l.c.*).

Some mixed aliphatic and aryl-aliphatic antimonials have also been prepared.

Tetramethyldistibine (antimony cacodyl), $Me_2Sb\cdot SbMe_2$.—Formed together with trimethylstibine by the action of the free methyl radical on films of antimony and obtained after fractionation as bright red needles melting at 17·5° to a pale yellow oil. Soluble in benzene, alcohol, ether, insoluble in water ; spontaneously combustible in air, and oxidised in solution to *dimethylstibinic acid*, Me_2SbO_2H. Solutions of bromine and iodine are decolorised with probable formation of dimethylstibine dihalides (Paneth and Loleit, J.C.S. 1935, 366).

Dimethylstibine chloride, Me_2SbCl.—Obtained by distilling trimethylstibine dichloride under reduced pressure, it is a colourless oil, b.p. 155°–160°/750 mm. Spontaneously inflammable at 40° ; its regulated oxidation leads to the *oxychloride*, Me_2SbOCl. Addition of chlorine gives the *trichloride* as white crystals, m.p. 105°–110° (Morgan and Davies, Proc. Roy Soc. 1926, **110A**, 523).

Dimethylstibine bromide, almost colourless crystals, m.p. 89°, b.p. 175°–180°/750 mm., and *iodide*, clear yellow flaky crystals, m.p. 86°, are prepared in a like manner (*l.c.*).

Dimethylstibine cyanide, $Me_2Sb\cdot CN$, a colourless crystalline compound, m.p. 113°–114°, is obtained by distilling *trimethylstibine cyanobromide* at 160° under 10 mm. pressure. Insoluble in water, readily so in ether or alcohol ; oxidised in air to the oxycyanide, $Me_2SbO\cdot CN$ (Morgan and Yarsley, Proc. Roy. Soc. 1926, **110A**, 534).

Dimethylstibine oxide, $[Me_2Sb]_2O$.—This antimony analogue of cacodyl oxide is produced on treating the dimethylstibine halides with alkalis or potassium carbonate. Colourless oil, spontaneously combustible in air.

Methylstibine dihalides, $MeSbX_2$, are prepared by heating the *dimethylstibine trihalides*, excepting in the case of the triiodide which is unstable and passes spontaneously into the primary product. *Dichloride*, colourless oil, b.p. 115°–120°/60 mm., also obtained by heating dimethylphenylstibine dichloride (Steinkopf, Schubart, and Roch, Ber. 1932, **65**, 409). *Dibromide*, greyish-white needles, m.p. 42°. *Diiodide*, bright yellow needles, m.p. 110° (Morgan and Davies, *l.c.*).

Tetraethyldistibine.—Formed by the action of free ethyl on warm films of antimony. Yellow oil decomposes at 155°, m.p. −61°. Oxidises in benzene solution to *diethylstibinic acid*, Et_2SbO_2H ; decolorises iodine and bromine to give the corresponding *dihalides* as yellow oils (Paneth and Loleit, *l.c.* ; Pearman and Paneth, J.C.S. 1935, 1154).

Diethylstibine iodide, Et_2SbI.—Made by treating the product from the action of antimony trichloride on magnesium ethyl bromide with hydrochloric acid and potassium iodide. Antimony triiodide is removed by washing with hydrochloric acid. Golden yellow flakes, m.p. 43° (Auger and Billy, Compt. rend. 1904, **139**, 509).

Syntheses of Aromatic Antimonials.

(I) Interaction of sodium with an aryl halide and antimony trichloride in benzene solution.—When heated for 24 hours with sodium a benzene solution of chlorobenzene and antimony trichloride yields triphenylstibine and its dichloride together with some diphenylstibine trichloride (Michaelis and Reese, Annalen, 1886, **233**, 45 ; Morgan and Vining, J.C.S. 1920, 777 ; B.P. 303092). The triarylstibine, which is the major product, may be converted into a mixture of the secondary and primary chlorides by heating with antimony chloride under pressure (Morgan and Micklethwait, *l.c.*). More recently Schmidt has extended such transformations so that the tertiary tervalent aryl antimonials may be made to pass successively into secondary and primary and *vice versa*. Thus triphenylstibine when heated with alcoholic hydrochloric acid in a stream of carbon dioxide gives diphenylstibine chloride, while diphenylstibine oxide is converted into phenylstibine oxide on heating in absolute formic or acetic acids. The primary state is the least stable and substances such as *m*-aminophenylstibine oxide readily eliminate antimony oxide and pass into secondary derivatives (Schmidt, Annalen, 1922, **429**, 123 ; G.P. 389151, 431202).

(II) Grignard Reaction.—Antimony trichloride when heated with magnesium aryl bromide or iodide gives the triarylstibine as the main product.

(III) The Diazo Synthesis.—The discovery in 1911 by the Chemische Fabrik von Heyden that antimony could be introduced into aromatic nuclei by means of the diazo reaction greatly facilitated the preparation of those primary stibonic acids the salts of which have become so important in chemotherapy. *Phenylstibonic acid* is so made by adding diazotised aniline with stirring to a cooled solution of antimony trichloride in aqueous sodium hydroxide. After some hours the acid is precipitated on acidifying the filtered solution with hydrochloric acid.

As a result of the researches of H. Schmidt and of the I.G. Farbenindustrie A.-G., the diazo synthesis has undergone many modifications. Instead of the original antimony trichloride it is now possible to use tartar emetic, while the alkali may be replaced by a tertiary base. It is possible also, and sometimes advantageous, to cause the reaction to proceed under neutral or acid conditions (G.P. 296940 ; B.P. 313058). Improved products are said to be obtained if polyhydric alcohols are added to the reaction mixture (B.P. 244746).

Aromatic Antimonials.

Triphenylstibine, Ph_3Sb.—Colourless triclinic plates, m.p. 53°, b.p. 231°–232°/16–18 mm., above 360°/760 mm. (with partial decomposition), d^{12} 1·4998. Synthesised by method (I) above, but is most conveniently obtained through the Grignard reaction, when the yields are almost quantitative (Morgan and Micklethwait, *l.c.*). May also be made from mono- or diphenylstibine oxides by heating at 180°–200° for 4 hours in an atmosphere of carbon dioxide.

In general, the triarylstibines are far more stable than the corresponding alkyl derivatives and show a lesser tendency to pass into the pentavalent state ; they do not form stibonium compounds with methyl iodide even at 100°.

Triphenylstibine dichloride.—Formed as a by-product in method (I) above, it is easily made by the direct addition of chlorine to triphenylstibine in petroleum. Colourless needles, m.p. 143°. Readily soluble in benzene and hot alcohol. *Dibromide*, needles, m.p. 216°. *Diiodide*, white plates, m.p. 153°.

Triphenylstibine oxide or hydroxide, Ph_3SbO or $Ph_3Sb(OH)_2$.—White crystalline powder, m.p. 212°, readily soluble in alcohol or acetic acid. Prepared either by hydrolysis of the dibromide with alcoholic potash or by oxidising triphenylstibine with hydrogen peroxide. If this oxidation is carried out in warm alkaline solution there is formed diphenylstibinic acid (G.P. 394795).

Triphenylstibine sulphide (*sulphoform*), Ph_3SbS.—White needles, m.p. 119°–120°. Originally prepared by careful action of hydrogen sulphide on an alcoholic ammonia solution of the stibine chloride, it is now made by direct addition of sulphur to triphenylstibine at 130°. A *selenide* is also known. Sulphoform has been used in the treatment of skin diseases (Kaufmann, Ber. 1908, **41**, 2761 ; G.P. 223694, 520306).

Diphenylstibine chloride, Ph_2SbCl.—Colourless crystals, m.p. 68°. Formed as a by-product in method (I) above ; it is also obtained by adding hydrochloric acid to a solution of the oxide in acetic acid (Michaelis and Günther, Ber. 1911, **44**, 2317 ; Grüttner and Wiernik, Ber. 1915, **48**, 1749 ; Schmidt, *l.c.*). Hydrolysed by sodium carbonate to the *oxide*.

Diphenylstibine trichloride.—Formed by addition of chlorine to the previous compound, it crystallises in colourless needles ($1H_2O$), m.p. 180°.

Diphenylstibinic acid, Ph_2SbO_2H.—Obtained by the hydrolysis of the trichloride or by the action of phenyldiazonium chloride on phenylstibinous oxide in the presence of alkali; white powder, m.p. 285°; soluble in dilute but not in concentrated hydrochloric acid; its solubility in alkalis depends on the method of preparation.

Phenylstibine dichloride, $PhSbCl_2$.—Colourless crystals, m.p. 62°, b.p. 290°, soluble in the usual organic solvents. Decomposes slowly, giving diphenylstibine chloride (Hasenbäumer, Ber. 1898, **31**, 2912; Schmidt, *l.c.*).

Series of aromatic antimonials similar to the above have been made containing various substituents in the benzene ring. In addition, antimony has been linked on to the diphenyl, α-naphthyl, 2-thienyl and camphoryl radicals.

Arylstibonic Acids.—The therapeutic development of antimony has tended to focus interest on the aromatic stibonic acids the salts of which have played such a prominent part in the successful treatment of certain tropical diseases. Such acids are generally amorphous, infusible solids, insoluble in water but dissolving in certain organic media. They are soluble in caustic alkalis, alkali carbonates and ammonia and the corresponding salts may be isolated. The original formula of Hausenbäumer for phenylstibonic acid, $PhSbO_3H_2$, represented these acids as derivatives of orthoantimonic acid, but it seems probable that they are better regarded as derivatives of the tri- and tetra-acids of Delacroix (Bull. Soc. chim. 1899 [iii], **21**, 1049; 1901 [iii], **25**, 288) and of Senderens (*ibid.* 1899 [iii], **21**, 53). They should thus be represented as $[3(ArSbO_2)H_2O]nH_2O$ or $[3(ArSbO_2)2H_2O]nH_2O$. This view is supported by the fact that the acids dissolve completely in $\frac{1}{3}$ of a molecular equivalent of alkali, giving solutions which, although initially neutral, soon develop an acid reaction and then require more of the base for neutrality which only becomes permanent after the addition of one molecular equivalent of the base. This slow neutralisation is regarded as being due to the hydration and consequent dissociation of the complex into three molecules of the simple stibonic acid.

Phenylstibonic acid, $[3(PhSbO_2)H_2O]2H_2O$.—Originally prepared by the hydrolysis of the tetrachloride, it is now made by the diazo synthesis (*v. supra*); white powder soluble in warm acetic acid and chloroform, and in cold mixtures of alcohol with benzene or ether. Soluble in concentrated hydrochloric acid, forming *phenylstibonic chloride*, $PhSbCl_4$, as slightly coloured crystals, m.p. 61°–65°. The tetrachloride forms *double salts* with ammonium chloride and amine hydrochlorides.

p-*Aminophenylstibonic acid* (stibanilic acid).—Manufactured by the diazo method from acetyl-*p*-phenylenediamine, the intermediate p-*acetylaminophenylstibonic acid* (Na salt=*stibacetin*) being hydrolysed by heating with dilute alkali. Although rather unstable, stibanilic acid is, nevertheless, the parent substance of most of the pentavalent antimony drugs. Diversity has been lent to it by the production of various salts and by substitution in the amino group and in the nucleus.

Salts of Stibanilic Acid.—*Diethylamine* p-*aminophenylstibonate*,

$$H_2N{\cdot}C_6H_4{\cdot}SbO_3H{\cdot}NH_2(C_2H_5)_2,$$

(*Neostibosan*; *v. Heyden* 693 or 693b).—Prepared by dissolving stibanilic acid in aqueous diethylamine and precipitating with acetone, it is a pale-coloured powder soluble in water, dilute alkalis, and acids. The alkaline solution gives an odour of diethylamine on warming.

Many similar salts have been made using methylamine, diethylaminoethanol, quinine, etc. (G.P. 485273, 502046, 555680; B.P. 311448; Niyogy, J. Indian Chem. Soc. 1928, **5**, 285).

Amino-substituted Derivatives of Stibanilic Acid.—*Urea Stibamine.*—Widely used in India, this drug is formed by the interaction of urea and stibanilic acid (Brahmachari, Indian J. Med. Res. 1922, **10**, 508; 1925, **13**, 111). Regarded at first as a simple urea salt, it was later thought to be *ammonium* 4-*carbamidophenyl stibonate*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SbO_3H(NH_4),$$

a substance which has been synthesised by Niyogy (J. Indian Chem. Soc. 1928, **5**, 753). Subsequently the detailed researches of Gray, Trevan, Bainbridge and Atwood proved urea stibamine to be a complex mixture containing not only the monocarbamide but also s-*diphenylcarbamido*-4 : 4′-*distibonic acid*,

$$[H_2O_3Sb{\cdot}C_6H_4{\cdot}NH{-}]_2CO,$$

which they have synthesised by the phosgenation of stibanilic acid. The therapeutic activity of urea stibamine is largely due to the 4 : 4′-distibonic acid (Proc. Roy. Soc. 1931, **108B**, 54).

Phenylglycineamide-p-*stibonic acid*,

$$(NH_2{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}Sb)_3O_2(OH)_2.$$

This analogue of tryparsamide is obtained from sodium stibanilate and either chloroacetamide or chloroacetic ester and ammonia. The *sodium salt* is a pale-coloured powder easily soluble in water to a clear neutral solution (Brahmachari, *l.c.*; Brahmachari and Das Gupta, Proc. Asiatic Soc. Bengal, 1930, **26**, 413).

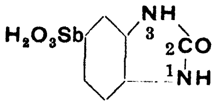
Other residues which have been introduced into the amino group are the hydroxyacyl- (B.P. 318491), carbo-alkoxy- (Hamilton and Etzelmiller, J. Amer. Chem. Soc. 1928, **50**, 3360), ω-methanesulphonic (U.S.P. 1766361) and glucosido- radicals (B.P. 234677). The sodium salt of the latter is the drug *Neostam.*

Azo Dyes from Stibanilic Acid.—These have been made by coupling diazotised stibanilic acid with phenols and amines. They have, however, no therapeutic value (Dunning and Reid, J. Amer. Chem. Soc. 1926, **48**, 2959; 1927, **49**, 2869; Riddell and Basterfield, Trans. Roy. Soc. Canada, 1929, **23**, III, 45; Mingoia, Gazzetta, 1932, **62**, 343).

Nuclear-substituted Derivatives of Stibanilic Acid.—m-*Chloro*-p-*acetaminophenylstibonic acid* (Na salt=*Stibosan* or *v. Heyden* 471).—Produced by the Chem. Fabr. v. Heyden in 1923, it has also been made by Niyogy (J. Indian Chem. Soc. 1927, **4**, 96, 397) from 3-chloro-4-acetylaminoaniline as a light brown powder. Niyogy has also obtained the m-*bromo*, m-*iodo*, and certain dihalogen derivatives.

Commencing with *m*-aminophenylstibonic acid many compounds have been made corresponding with those from stibanilic acid; their therapeutic activity seems, however, to be inferior (Fargher and Gray, J. Pharm. Exp. Ther. 1921, 341; Morgan and Cook, J.C.S. 1930, 737; Balaban, J.C.S. 1930, 1685; G.P. 510451; B.P. 226686).

Miscellaneous Stibonic Acids.—*Benziminazolone-5-stibonic acid.*—Prepared either by the diazo process from 5-aminobenziminazolone or by the phosgenation of *o*-phenylenediaminestibonic acid; colourless powder soluble in dilute alkalis and organic bases. The 1-*methyl*, 1-*ethyl*, and 7-*chloro* derivatives have also been made (B.P. 343072, 343744).



2-*Hydroxypyridine-5-stibonic acid.*—Yellowish-brown powder, sparingly soluble in alcohol; it is prepared in the usual manner from 2-hydroxy-5-aminopyridine, being purified by conversion into the *stibinopyridine*, which is then oxidised back to the acid (B.P. 250287).

Quinolyl-5-stibonic acid.—Obtained from the corresponding aminoquinoline as a buff powder, soluble in dilute acids and alkalis, and purified through the *stibonic chloride hydrochloride* (m.p. 222°).

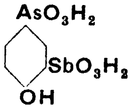
Similar acids have been made containing the antimony in the 3-, 6-, 7-, and 8-positions respectively. 2-*Hydroxyquinolyl-6-stibonic acid* has also been prepared (Morgan and Cook, *l.c.*; Sen and Mukherjee, J. Indian Chem. Soc. 1934, **11**, 541).

Acridone-3-stibonic acid.—Formed in the usual manner from 3-aminoacridone; light brown powder soluble in dilute alkalis, the solutions showing a weak purple-blue fluorescence (Barnett, Gillieson and Kermack, J.C.S. 1934, 433).

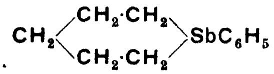
Distibonic Acids. — *p-Phenylenedistibonic acid*, $H_2O_3Sb{\cdot}C_6H_4{\cdot}SbO_3H_2$, is a buff powder obtained by the diazo process on *p*-phenylenediamine (Riddell and Basterfield, *l.c.*; Mistry and Guha, J. Indian Inst. Sci. 1932, **15** [A], 25). The latter have prepared a number of di- and polystibonic acids.

Stibonic-Arsonic Acids.—Acids of the type $C_6H_4(SbO_3H_2)(AsO_3H_2)$ may be prepared either by acting with antimony oxide on diazotised aminophenylarsonic acids or with an arsenite on the aminophenylstibonic acids. Such substances are more closely allied to the stibonic than to the arsonic acids. They are not readily soluble in alkalis, the rate of solution varying with the concentration of hydroxyl ions, the nature of the alkali, temperature, and the age of the compound. They exhibit the phenomenon of gradual neutralisation and they form double compounds with ammonium chloride and pyridine hydrochloride in concentrated hydrochloric acid.

4-*Hydroxyphenylene-1-arsonic-3-stibonic acid.*—Made by the action of antimony oxide on diazotised 3-amino-4-hydroxyphenylarsonic acid. During the preparation the diazo compound crystallises out as a yellow diazophenol (1-arsonic-3:4-*ortho*benzoquinone-3-diazide). Faintly coloured powder insoluble in the usual media but soluble in alkalis and concentrated hydrochloric acid. Like the hydroxy- and alkoxy-stibonic acids it slowly loses antimony on keeping (Schmidt, Ber. 1924, **57**, 1142; B.P. 357061).



Cyclic Antimonials. — *Phenylcyclopentamethylenestibine.*—Prepared from phenylstibine dichloride and the magnesium compound of αε-dibromopentane; colourless, viscous, unpleasant-smelling oil, b.p. 169°–171°/18–20 mm. (in CO_2); oxidises on exposure to air (Grüttner, Wiernik, and Krause, Ber. 1915, **48**, 1473; 1916, **49**, 437).



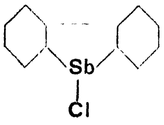
$$CH_2\begin{matrix}\diagup CH_2{\cdot}CH_2 \diagdown \\ \diagdown CH_2{\cdot}CH_2 \diagup\end{matrix}SbC_6H_5$$

The corresponding *methyl* derivative, b.p. 73°–73·5°/17 mm., forms a *dichloride* which decomposes at 160°–185° into methyl chloride and cyclo-*pentamethylenestibine chloride*, b.p. 110°–111°/13 mm. (Steinkopf, Schubart and Roch, *l.c.*).

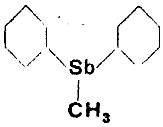
Xenylene-2 : 2′-stibine chloride (I).—This antimony analogue of carbazole is prepared either by the abstraction of water from *xenyl-o-stibonic acid* ($C_6H_5{\cdot}C_6H_4{\cdot}SbO_3H_2$) followed by reduction in the presence of hydrochloric acid, or by heating *xenyl-o-stibine dichloride* under reduced pressure, when hydrogen chloride is evolved. Greenish-white acicular crystals, m.p. 209°, moderately soluble in organic solvents. With sodium iodide in acetone it forms the *iodide*, lemon-yellow needles, m.p. 222°.

2 : 2′-*Xenylenemethylstibine* (II).—Obtained by the action of methyl magnesium iodide on the foregoing stibine iodide. Yellowish-white leaflets, m.p. 57°; addition of bromine gives the *dibromide*, m.p. 207°. *Di-o-xenylstibine chloride* $(C_6H_5{\cdot}C_6H_4)_2SbCl$. This secondary antimonial is formed by the successive action of warm alkali and hydrochloric acid on xenyl-*o*-stibine dichloride, the oxide *tetrakis-o-xenylstibine oxide*, $[(C_6H_5{\cdot}C_6H_4)_2Sb]_2O$, m.p. 157°, appearing as an intermediate. The chloride forms colourless needles, m.p. 125·5°, while the *iodide* occurs as yellow prisms, m.p. 156°–157°. Addition of chlorine to the chloride gives the *trichloride* as small colourless needles, m.p. 177°.

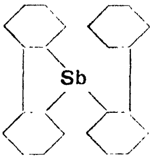
2 : 2′-*Xenylene-o-xenylstibine dichloride* is obtained as small white nodules, m.p. 212°, when the above trichloride is warmed *in vacuo*. When heated with zinc dust it yields the tertiary *stibine* (III) which crystallises in large rosettes of colourless needles, m.p. 106°–107°, fairly soluble in most organic media (Morgan and Davies, Proc. Roy. Soc. 1930, **127A**, 1).



I.



II.



III.

Stibacridinic acid (IV).—Obtained as a pale-coloured powder when *diphenylmethane-2-stibonic acid* is heated with acetic anhydride containing a little sulphuric acid and the product poured into water ; it is easily soluble in chloroform.

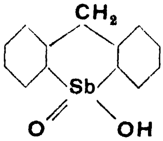
10-*Chloro*-9 : 10-*dihydrostibacridine* (V).—Reduction of stibacridinic acid in hydrochloric acid yields the chloride as colourless needles, m.p. 105°, readily soluble in most organic media. The corresponding *bromo-* and *iodo-* derivatives have also been made.

10-*Methyl*-9 : 10-*dihydrostibacridine* (VI).—Prepared by the action of methyl magnesium iodide on the foregoing 10-iododihydrostibacridine ; beautiful colourless spangles, m.p. 101°.

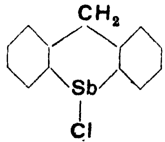
Bis-2-diphenylmethanestibine chloride,

$$(C_6H_5{\cdot}CH_2{\cdot}C_6H_4)_2SbCl,$$

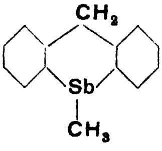
is formed by the successive action of warm alkali and hydrochloric acid on *diphenylmethane-2-stibine chloride* ; slender hair-like needles, m.p. 87·5°. The corresponding *trichloride* loses hydrogen chloride on heating *in vacuo*, giving 10-(2-*diphenylmethane*)-9 : 10-*dihydrostibacridine dichloride* (VII) ; colourless plates, m.p. 127° ; easily soluble in most solvents excepting alcohol and petroleum (Morgan and Davies, Proc. Roy. Soc. 1933, **143A**, 38).



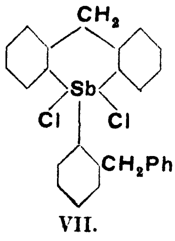
IV.



V.



VI.



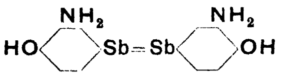
VII.

STIBINOBENZENES.

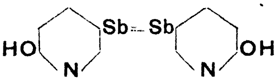
The members of this series contain the group $-Sb{=}Sb-$ and are obtained by the reduction either of the corresponding stibonic acids or of the stibine chlorides with sodium hyposulphite or hypophosphite. They are coloured amorphous solids insoluble in water and very susceptible to oxidation.

Stibinobenzene, $C_6H_5{\cdot}Sb{=}Sb{\cdot}C_6H_5$.—Pale yellow powder, soluble in glacial acetic acid or chloroform, prepared by reducing phenylstibonic acid with sodium hyposulphite and extracting the crude product with a mixture of alcohol and benzene containing copper powder. Alkaline hydrogen peroxide regenerates the original stibonic acid.

3 : 3′-*Diamino*-4 : 4′-*dihydroxystibinobenzene*.—This antimonial analogue of salvarsan base is obtained as a reddish-brown precipitate on reducing 3-nitro-4-hydroxyphenylstibonic acid in the usual manner. It is easily acylated and it condenses with aldehydes. The amino- groups can be diazotised, while the hydroxy- radicals produce a coloration with ferric chloride (G.P. 268451).



2 : 2′-*Dihydroxy*-5 : 5′-*stibinopyridine*. — Reduction of 2-hydroxypyridine-5-stibonic acid with hypophosphorous acid yields the stibinopyridine as a yellow powder which does not appear to be appreciably soluble in any solvent (B.P. 250287).



Tetraphenyldistibine, $Ph_2Sb{\cdot}SbPh_2$.—This secondary stibinobenzene is formed when diphenylstibine iodide is reduced with sodium hypophosphite in aqueous alcohol and in the absence of oxygen ; pale yellow-green needles, m.p. 121°–122° ; it readily absorbs oxygen to form a peroxide $[(Ph)_2SbO-]_2$; with iodine it regenerates the diphenylstibine iodide.

Tetra-p-tolyldistibine has also been made (Blicke, Oakdale, and Smith, J. Amer. Chem. Soc. 1931, **53**, 1025 ; 1933, **55**, 1198).

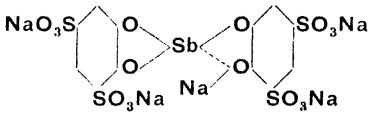
ANTIMONYL COMPOUNDS.

Although not true antimonials, this class deserves some mention because of its importance in chemotherapy.

Antimonyl tartrates.—The discovery of the efficacy of tartar emetic in the treatment of bilharziasis and other tropical diseases has led to the search for other salts less toxic than the potassium. Amine salts have been specially favoured and antimonyl tartrates of ethylenediamine, urea, novocaine, apothesine, quinine, etc., have been produced (Fargher and Gray, J. Pharm. Exp. Ther. 1921, **18**, 348 ; Brahmachari, Ind. J. Med. Res. 1923, **11**, 406 ; Christiansen and Norton, J. Amer. Chem. Soc. 1925, **47**, 876).

Antimonyl derivatives of other aliphatic hydroxy- or thiocarboxylic acids have also been made. To the latter series belong the therapeutically important antimony thioglycollates and thioglycollamides.

Derivatives of polyhydroxy phenols.—Although antimonyl polyphenols have long been known, recent work has considerably extended the field, some very complex substances having been produced. Most important in this class is *sodium antimonylpyrocatecholdisulphonate* (*Neoantimosan, Fouadin*), produced by the action of antimony oxide on sodium pyrocatecholdisulphonate in the presence of excess of alkali; a colourless powder, easily soluble in water, the solution remaining clear on addition of dilute acid or alkali (B.P. 213285). Its formula is given as



Polyphenol antimony compounds may also be made by using arylstibine oxides in place of antimony oxide (B.P. 419742). Further variations are obtained by treating these substances with aliphatic hydroxycarboxylic acids, thioglycollic acid, or hydrogen peroxide.

Miscellaneous antimonyls.—Antimony oxides also form complex compounds with sugars, sugar acids (*e.g.* gluconic acid), and aliphatic polyvalent alcohols. Such substances are soluble in water and the solutions are fairly stable (B.P. 343898, 352928; G.P. 525651).

CHEMOTHERAPY OF ANTIMONY.

Derivatives of antimony have proved themselves to be sovereign remedies in the treatment of both schistosomiasis (bilharziasis) and leishmaniasis (especially kala-azar). Both these diseases are very widespread and therefore the value of such drugs can hardly be assessed, but some indication may be obtained from the fact that without treatment the death-rate from kala-azar is over 90%, whereas with treated cases this is reduced to below 10%.

Although tartar emetic was found to give beneficial results in both these diseases, yet its considerable toxic effects made it imperative to obtain other derivatives which should be better tolerated while having, if possible, a greater toxicity towards the parasites. Furthermore, owing to necrosis, tartar emetic could only be injected intravenously and was thus unsuitable for mass treatment; the ideal drug should be capable of oral or intramuscular administration. This investigation has proceeded on two lines:

(*a*) A search for more stable complex tervalent antimonyl compounds which has resulted in neoantimosan, antimony thioglycollamide, etc.

(*b*) The use of aryl quinquevalent derivatives such as stibosan, neostibosan, urea-stibamine, neostam, etc.

It is curious that in bilharziasis the best results seem to be provided by the tervalent antimonyl compounds, whereas the quinquevalent antimonials are more effective in kala-azar. In general the former are somewhat more toxic than the latter, but this is of little consequence in the treatment of schistosomiasis, where the amount of antimony injected is comparatively small and the period of treatment is short. In kala-azar, however, secondary effects are very undesirable owing to the much longer period of treatment. Even so, many of these drugs do show toxic reactions, and in this respect neostibosan seems to be the most promising of such substances. Large doses can be administered intramuscularly, and in consequence the period of treatment, which was about 3 months with tartar emetic, has been reduced to 8 days with neostibosan.

Urea stibamine, neostam, stibosan and the antimony analogue of tryparsamide have also been successfully used in India.

Bibliography.—"Organic Compounds of Arsenic and Antimony," G. T. Morgan, London, 1918; "Organic Derivatives of Antimony," W. G. Christiansen, New York, 1925; "Recent Advances in Chemotherapy," G. M. Findlay, London, 1930; "Text-book of Inorganic Chemistry," edited by J. Newton Friend, vol. XI, part iii, A. E. Goddard, London, 1936.

G. R. D., G. T. M.

ANTIMONINE. Trade name for antimonyl calcium lactate, used as a tannin-fixing mordant,

$$(SbO\cdot C_3H_5O_3)_2Ca_3(C_3H_5O_3)_4 2C_3H_6O_3$$

ANTIMONITE. Native antimony sulphide (*v.* ANTIMONY).

ANTIMONY (*Antimoine*, Fr.; *Antimon*, Ger.). *Stibium*. Sym. Sb. At. wt. 121·76. At. no. 51. The early history of antimony has been dealt with by H. Hyman (J.S.C.I. 1924, **43**, 1006).

Occurrence.—Antimony occurs native in small quantities and also as *arsenical antimony* or *allemontite*, AsSb.

Combined with *oxygen* as the sesquioxide, Sb_2O_3, it occurs in *antimony bloom, white antimony*, or *valentinite* (orthorhombic) and in *senarmontite* (cubic). In *antimony ochre* or *cervantite* and in *stibiconite* and *volgerite* it occurs as Sb_2O_4, and in *stiblite* as Sb_2O_4,H_2O.

Combined with *sulphur* it occurs as *stibnite, antimonite*, or *antimony-glance*, Sb_2S_3. In union with *sulphur* and *oxygen* together it forms *red antimony, antimony blende*, or *kermesite*, $2Sb_2S_3,Sb_2O_3$.

In combination with metals there are *antimonial silver* or *discrasite*, Ag_3Sb, and *antimonial nickel* or *breithauptite*, NiSb.

With *sulphur and metals* antimony forms a number of *sulphantimonites*, among which may be mentioned *boulangerite*, $5PbS,Sb_2S_3$, *jamesonite*, $2PbS,Sb_2S_3$, *berthierite*, FeS,Sb_2S_3, *pyrargyrite* or *red silver ore*, $3Ag_2S,Sb_2S_3$, *wolfsbergite* or *antimonial copper*, Cu_2S,Sb_2S_3, *bournonite*, $3(Pb,Cu_2)S,Sb_2S_3$, *ullmannite* or *nickeliferous grey antimony*, NiSbS. Antimony is also found in small quantities in certain ferruginous waters, iron ores, coal formations and river sands.

The antimony minerals of commercial importance as ores are *stibnite* and the decomposition products which are usually associated with it and sometimes entirely replace it, viz. *kermesite*, *valentinite*, *senarmontite*, and *cervantite*.

Antimony is widely distributed and its ores occur in workable quantities in some 14 to 16 countries, including, in approximate order of output, China, Mexico, Bolivia, Czechoslovakia, France, Algeria and Italy. Small quantities of the ores have been found in many other countries and stibnite has been discovered in Cornwall, Cumberland and Scotland.

By far the largest proportion of the world's supply of antimony is derived from China, chiefly from the province of Hunan. This country supplies about 20,000 tons annually at a cost below that of its competitors and it appears to be destined to remain the chief producer for many years, as estimates have given 1,300,000 tons of metal still available in these deposits, with an additional 150,000 tons of metal in ores at present of too low grade to be mined (H. F. Bain, "Ores and Industries of the Far East," 1927, p. 151). The Chinese industry, being well established, was able to respond rapidly to the great demand of the Great War, exports increasing from 12,822 tons of crude and refined antimony and regulus and 4,281 tons of ore in 1913, to 34,410 and 3,798 tons respectively in 1917. The ore, remarkable for its purity, occurs as pockets mainly of stibnite in a flat bed of dolomitic limestone. An export monopoly formed in China by the Hunan Antimony Syndicate caused the c.i.f. price of the metal to rise from £21 10*s*. per ton in January 1934 to £58 per ton in December of the same year, and this has had the effect of developing the work of producers in other countries and especially that of a smelter in U.S.A. which draws its supplies of ore from Mexico.

France is the most important antimony-producing country in Europe and also controls important productive deposits in Algeria.

Under normal conditions the potential supply of antimony is far in excess of the demand and consequently only those deposits which can be cheaply worked and are favourably situated with regard to markets, or contain appreciable quantities of other minerals, especially gold, have been extensively developed.

By far the most general ore of antimony is stibnite, but in some cases the oxide is found in workable quantities and in other cases both oxide and sulphide occur together.

EXTRACTION OF ANTIMONY.

Antimony ores are extremely difficult to concentrate mechanically owing to the large amount of slime produced ; flotation processes have, however, been used with success ; for example, C. S. Parsons (Dept. of Mines, Ottawa, Canada, Mem. Series, September, 1924) has successfully concentrated the Lake George stibnite ore by flotation in a callow unit consisting of two "rougher" cells and two "cleaner" cells of the new flat-bottom type. The reagent used consisted of a mixture of 40% coal-tar and 60% coal-tar creosote. For every ton of ore, 5 lb. of sulphuric acid was used. At the Costerfield antimony smelter (J. M. McLean, Chem. Eng. Min. Rev. 1926, **19**, 93) a combination of jigs, tables, and flotation has been adopted for concentration.

Metallic antimony and its compounds are nearly always extracted from the ores by dry methods. According to their suitability for the several methods of treatment, the ores fall into two broad classes :

(*a*) Sulphide ores containing over 40% stibnite.

(*b*) Sulphide ores containing less than 40% of the sulphide, and oxide ores of any grade. In this class also may be included liquation residues and flue deposits, etc.

Preliminary Treatment of Ores.—Ores of class (*a*) are used for the production of the metal by the English process. If the content of sulphide is over 90%, the ore requires no preliminary treatment, but less pure ore is subjected to a process of *liquation*, in which the sulphide is melted and allowed to run away from the gangue.

The following method of liquation was formerly used where fuel was plentiful. The ore was placed in small lumps in a number of conical pots of 45 kg. capacity, each perforated below and standing on a perforated plate over a sunken receiver. The pots were surrounded by fuel which continued to burn for 10 hours, the melted sulphide, known as crude antimony, collecting in the receivers.

In some cases the pots are replaced by cylindrical tubes, perforated below and standing on similarly perforated plates above the receivers. Each cylinder has a capacity of 500 lb. of ore, four being heated in one furnace. Each has a hole at the side, through which the residues are removed, these holes being closed during the heating. The receivers are of clay, or of iron coated with clay.

At Chang-Sha, and also in other parts of the province, crude antimony is obtained from high-grade (58%) ores by liquation. The process is carried out in furnaces each of which holds two clay crucibles, the charge for each crucible being 50 lb. of ore. The crucibles are inclined and perforated at the bottom ; they are fired for two hours, the liquated sulphide collecting in a cavity at the back of the furnace, whence it is ladled into iron moulds and allowed to solidify. The pasty liquation residue is dumped into loose iron frames formed of two L-shaped pieces, in which it cakes together on cooling (Schoeller, J.S.C.I. 1913, **32**, 260).

The method of liquation in reverberatory furnaces is used in some places where ore can be mined cheaply but fuel is dear. The consumption of fuel per unit of sulphide liquated is least with this type of furnace, but there is a considerable loss of antimony by volatilisation. This loss, however, can be prevented by the use of suitable condensing apparatus such as that of Herrenschmidt (*v. infra*).

In any process of liquation the temperature must be carefully regulated, as too low a temperature results in a low yield of sulphide, the residues containing too much antimony, while too high a temperature increases the loss by volatilisation.

The liquation process as conducted in

pots, tubes, and crucibles is considered to be laborious, expensive and wasteful, and although this operation can be carried out in reverberatory furnaces, it is attended with considerable difficulties. The maintenance of a reducing atmosphere is not easy with furnaces fired with solid fuel, and gas-firing does not seem to have been fully developed.

The liquated stibnite contains much less sulphur than is required by the formula Sb_2S_3, and Schoeller has shown that this is due to the presence of oxygen.

Ores of class (*b*) are either roasted to the non-volatile tetroxide, or to the volatile trioxide, or are subjected to one of the direct reduction processes.

The oxidation of the sulphide to tetroxide takes place at temperatures between 350° and 400° in presence of excess of air. If the ore is impure, antimonates of the metallic impurities are formed at the same time. During the roasting there is a great tendency for the ore to frit, and this necessitates the constant rabbling of the charge. The presence of gangue renders the ore less liable to fuse, so that the process is most easily carried out with poor ores, *e.g.* ore-dust, for the treatment of which it is largely used. The furnaces employed are of two classes :

(*a*) Hand rabbled reverberatory furnaces, having an egg-shaped flat bed, with a fire-place on either side and a working door at the front. With these the process is intermittent.

(*b*) Long bedded furnaces, in which the roasting is carried on continuously. These furnaces are 40–45 ft. long, by 8 ft. wide, by 2 ft. high, and have 10 working doors on each side. The ore is charged in at one end, and is then gradually worked along the bed during about 40 hours, and finally discharged at the other end. Fresh ore is continually charged into the furnace at the rate of 6 cwts. every 8 hours.

In the dead roasting process for the preparation of the stable tetroxide, difficulties are met with in reverberatory furnaces owing to the fritting of the charge, and a cylindrical rotating furnace, 38–66 ft. in length, fired by long-flaming coal or, preferably, by gas has been used by A. Lissner and R. Eichelter (Metall u. Erz, 1922, **19**, 373).

The oxidation of the sulphide to volatile trioxide takes place at about 400° with a carefully regulated amount of air. This process, provided suitable condensation apparatus is installed, presents marked advantages, and is finding an increasing application, especially in dealing with poor ores. It may be noted that arsenic is completely separated as the more volatile oxide, that any gold or silver present is left in the residue and can afterwards be extracted, that the loss of antimony and the consumption of fuel are low. Many different forms of plant have been used for this process, but in most the roasting takes place in a furnace of cupola type, the most important processes being the Chatillon and Herrenschmidt.

In the Chatillon process the volatilising-roasting of the ore is conducted in a furnace made up of two double cupolas, rectangular in cross section. The two upper furnaces open into a flue which is common to both and terminates in the downtake through which the fumes are led to the condensing plant. Within the walls of the upper cupolas are vertical flues which communicate with the lower cupolas.

Each of the lower cupolas is fitted on two sides with inclined bars forming grates, the other sides being of fire-brick, thus forming a hopper. The bottom is closed by a plate of iron, on opening which the spent residue drops into a truck below.

Each furnace is charged with ore in lumps or as dust, and coke in alternate layers, and is penetrated by hot air from the lower cupolas ; the sulphide is thus oxidised and volatilised as Sb_2O_3. The function of the lower cupolas is to receive the residues from the upper cupolas, to complete the oxidation of any undecomposed sulphide and the extraction of the Sb_2O_3, and at the same time to cool the residue and heat the air supply to the upper cupolas.

In the Herrenschmidt process the roasting furnace is a rectangular shaft of fire-brick with a step grate of iron bars, and is provided with a hopper through which the ore, mixed with 4–5% of gas-coke or 6–7% charcoal, is introduced. The gases pass from the furnace into a chamber, and then through a series of cast-iron tubes placed nearly vertical and air-cooled, in which the main portion of the trioxide is deposited. The last traces are removed by forcing the gases up a tower filled with coke over which water flows. The draught is maintained by two centrifugal fans, working tandem. It is stated that 6 tons of ore, containing 10–15% antimony, can be treated in 24 hours, with a yield of over 90%.

Of these volatilisation processes the Herrenschmidt furnace is chiefly used in China, as it is simple in construction and easy to manipulate. In France the Chatillon furnace is mostly used, and this has a distinct advantage in its suitability for the treatment of ore dust and its capacity for the conservation of heat.

Other processes for the production of the trioxide use cylindrical rotating furnaces, A. Lissner and R. Eichelter (*l.c.*) having revived the idea of Plews by adopting a furnace 38 ft. in length, with gas firing. Converters have also been used for the volatilisation process, and are especially suitable for the treatment of fine ores and ores of a calcareous nature (C. Y. Wang, Proc. World Eng. Cong. Tokyo, 1929, **35**, 185).

For the condensation of the trioxide the following methods are used :—

(i) Condensation pipes.
(ii) Condensation chambers with or without running water on the outside surface.
(iii) Coke towers.
(iv) Bag filters.
(v) Electrical precipitators.

The condensation system is invariably composed of two parts : first the condensation pipes and chambers ; and second, the coke towers, the bag filters, or the electrical precipitator.

After passing through the condensation pipes and chambers at least 25% of the oxide originally present in the gas remains, and after passing through coke towers at least 10% is left, and although largely used in China, coke towers invariably prove to be inefficient. Bag filters are more efficient, but a large installation is required, and the renewal of bags becomes troublesome and expensive. As an adjunct to the bag filters the Waring Dust Collector (Mining Mag. 1928, **39**, 352) is used. The main feature of this cyclone separator is that the gas laden with particles is broken up into a large number of small currents meeting each other so as to destroy almost entirely their original high velocity and thus causing deposition of dust.

The Cottrell process of precipitation of fume is most efficient and, except for small and isolated smelters, should displace coke towers and bag filter systems. The precipitator at the smelter of the Société Nouvelle des Mines de la Lucette à la Genest in France is composed of two compartments, each containing 16 tubes of 30 cm. internal diameter and 4·8 m. in length; in the middle of each tube a negative electrode of nichrome wire 2 mm. in diameter is passed. The gas treated contains on an average 10 g. of oxide per cu. m., which after passing through the apparatus is reduced to 5–10 mg. per cu. m., showing only an insignificant loss.

Smelting of the Metal.—Antimony is prepared from "crude antimony" or high-grade stibnite ores by the "English" or "precipitation" method. The ore, of which the composition has been determined by analysis, is ground under edge-runners to the size of a hazel-nut, or smaller, and is subjected to three operations :

Singling.—This process is carried out in crucibles, of which about forty are arranged in a double row on the hearth of a long reverberatory furnace having a grate at each end and a flue, leading to condensing chambers, in the middle. The crucibles are about 20 in. high and 11 in. across, and are made of a mixture of 6 parts fire-clay and 1 part plumbago. The charge for each pot is 42 lb. ore, 16 lb. iron, 4 lb. salt, and 1 lb. slag from "doubling" (*v. infra*). These materials are introduced into the red-hot crucible, and kept in a state of fusion for 2–3 hours, at the end of which time the contents are poured into moulds, and the antimony is removed from beneath the slag. The product, known as *singles*, usually contains about 91% antimony.

Doubling is carried out in crucibles arranged in a furnace as previously described. The charge for each pot is 84 lb. broken singles, 7–8 lb. liquated sulphide, and 4 lb. salt, and the fusion, which takes about 1½ hours, is closely watched, the workman judging from the nature of the slag when the operation is complete. The slag is then removed with an iron ladle and the metal poured into moulds. This product is called *bowl metal* or *star bowls*, and sometimes contains over 99% antimony.

Starring, or *melting for star metal* (*v. infra* under *Refining*).

In the English process the loss due to slagging and volatilisation is small, being only 2–5%.

It is possible also to reduce the sulphide on the hearth of a reverberatory furnace. The partially roasted ore, which contains the sulphide and oxides of antimony, is mixed and fused with 8–13% of coal and 9–11% of soda, frequently with the addition of iron, in which case the slag produced is much less fusible and does not entirely cover the bath of metal ; the antimony produced also contains much iron. Where carbonate of soda is used for the fusion the mass froths considerably and attacks the furnace hearth.

The metal is prepared from either of the oxides by one of the numerous reduction processes now in use.

(*a*) Reduction in reverberatory furnaces is carried out in gas-fired furnaces in which the furnace-bed is egg-shaped, deep in proportion to its width, and is provided with a tap-hole at the lowest point. The furnace gases are passed through a long series of condensing chambers. First 90–110 lb. flux (chiefly soda and sodium sulphate) and 220–230 lb. of slag from a previous operation are melted on the hearth, and then 400–500 lb. of roasted ore and 67–75 lb. of charcoal are added, and the whole kept in a state of fusion until reduction is complete.

(*b*) The direct smelting of natural oxide ores of antimony has been carried out at Wadley, Mexico, and roasted sulphide ores and briquetted oxides can also be smelted in water-jacketed blast-furnaces.

(*c*) Reduction in crucibles is only used when rich ore or the trioxide is available. The reducing agent for the trioxide is carbon (charcoal or anthracite), and sodium sulphate and carbonate are added to form a slag.

(*d*) The direct reduction of the volatile trioxide, as it issues from the roasting furnaces, by means of producer gas, water gas or acetylene has been experimented upon by R. Jahn (Montanistische Rundschau, 1925, **17**, 565). The metal thus produced falls in exceptionally fine particles into the reduction chamber and is claimed to be free from arsenic.

Considerable quantities of antimony ore are now treated directly for the production of the metal.

W. R. Schoeller (Trans. Inst. Min. and Met. 1917–18, **27**, 237) describes the blast-furnace smelting of antimony ores direct in water-jacketed blast-furnaces, the charge consisting of ore, basic slag, chalk, and coke. In this method no iron is added to the charge and no reduction of iron takes place in the furnace. The antimony is obtained as a high-grade metal, practically free from iron. The best conditions for working the furnace are found to be about 10% coke, low blast pressure, low metal content of charge (about 10%), high smelting column (over 15 ft.), and provision of a heated forehearth for the separation of metal and slag.

Electric furnaces have been applied to the smelting of antimony ores. The process suggested by C. G. Fink (Amer. Electrochem. Soc. 1912, **21**, 452) is based on the reaction

$$Sb_2S_3+3CaCO_3+6C=3CaS+9CO+2Sb$$

which is carried out in a vacuum electric furnace at 600°–700°, this temperature being afterwards raised to 1,300° for the volatilisation of the antimony which is collected. An electric furnace method has been patented by A. Germot according to which high-grade antimony ore is dissociated at about 1,500° into antimony metal and sulphur (C. Y. Wang, Proc. World Eng. Cong. Tokyo, 1929, **35**, 189).

Among processes allied to the smelting of antimony there need only be mentioned that of Herrenschmidt for the extraction of gold from antimony (Fr. Pat. 350013, 1904). This depends on the fact that when a small quantity of antimony is melted with or reduced from auriferous stibnite, all the gold present in the sulphide passes into the metal.

Many proposals have been made for the extraction of antimony by wet or electrolytic methods, but they have not been a success commercially.

REFINING OF ANTIMONY.

Unrefined antimony contains sulphur, iron, arsenic, and sometimes copper, gold and lead. The following analyses show the composition of typical samples, I and II being metal made with scrap iron ; III and IV metal from roasted ore smelted in a blast-furnace ; V Chinese :

	I.	II.	III.	IV.	V.
Antimony.	94·5	84·0	97·2	95·0	98·20
Iron . .	3·0	10·0	2·5	4·0	0·146
Sulphur .	2·0	5·0	0·2	0·75	0·37
Arsenic .	0·25	1·0	0·1	0·25	0·148
Gold . .	traces	—	—	—	—

All these impurities, except lead, can be removed by slagging with oxidising, sulphurising, or chlorinating agents. The usual fluxes are : Glauber salt and charcoal, which remove copper and iron as sulphides, and arsenic as sodium arsenate ; and antimony glass (antimony oxysulphide), which eliminates sulphur. Chlorides, such as salt or carnallite, must be used with caution, or great loss by volatilisation may result.

A " glass of antimony " is prepared by fusing a mixture of the crystalline antimony oxide which collects on the hotter portions of the flues with sulphide of antimony, until it forms a glassy dark grey or brown mass ; this is mixed with carbonate of soda for the purification of the metal, and is occasionally used alone when the metal is but slightly impure.

Refining in crucibles finds its chief application in the English process. The " star " bowls (*v. supra*) are cleaned from slag by chipping with sharp hammers, the metal is then broken small and melted with 2–3% of antimony flux, prepared by melting together American potashes and powdered stibnite in varying proportions (approximately 3 parts potashes and 2 parts stibnite) until, by experiment, the correct composition is found. The refining is carried out in the pots nearest the grates, and takes 30 minutes to 1 hour, the charge for each crucible being 84 lb. The finished product is run into 8-lb. ingots, which are carefully covered with slag and allowed to cool without disturbance. The coal consumption is large, but is compensated by a much smaller loss by volatilisation than occurs in other processes.

Refining in reverberatory furnaces is carried out in large-scale works.

The bed of the furnace is heated to a cherry red and the crude antimony is placed on it ; a quantity of oxide and some arsenic escape, and in from 30 to 60 minutes the metal has run down. From 3 to 7% (according to the purity of the metal) of carbonate of soda, sometimes mixed with coal or coke, is then added. The metal is thus covered and fumes less, small jets of flame appearing occasionally on its surface ; the temperature is raised, the metal remaining under the slag for from 1 to 3 hours (determined by the workman); the slag then becomes thick, and is removed by drawing it through the door with a long-handled flat transverse iron.

3% of antimony sulphide and 1½% of oxide are then thrown on the surface of the metal, and when melted 4½% carbonate of potash, or of a mixture of carbonate of potash and soda, is added, or glass of antimony may be used. By this means the iron and last traces of sulphur are removed ; in less than 15 minutes the refining is complete, and the critical operation of ladling is performed. A cast-iron hemispherical ladle, holding 15–20 kg., is riveted to a chain hanging from the roof exactly in front of the working door, before which the cast-iron moulds for receiving the metal are arranged on a stone table. The workman dips his ladle obliquely, removing some slag with the mètal ; part of this is first poured into the mould to prevent the metal from actually touching the mould, and the metal is well covered with the slag and left at rest. Unless this be done the " starring " will be imperfect, and, as this is considered a test of purity, its value will be lowered in the market. The slag may generally be used again. The oxide condensing in the flues is removed as seldom as possible as this operation, as well as the furnace work, is very injurious to the workers.

Star antimony usually contains small amounts of iron, lead, sulphur and arsenic, but can be further purified by Liebig's method, which consists in fusing the metal successively with 12% sodium carbonate and 6% antimony sulphide, and again with sodium carbonate to which a little nitre has been added.

The following are typical analyses of commercial antimony (*v.* Min. and Sci. Press, 1915, **111**, 53).

	Cookson's.	Hallett's.	Japanese.	Chinese.
Lead .	0·041	0·669	0·424	0·018
Tin . .	0·035	0·175	0·012	0·035
Arsenic .	trace	trace	0·095	0·017
Copper .	0·040	0·038	0·043	0·008
Iron . .	0·010	0·014	0·007	0·007

When " pure," and cast under correct conditions, a beautiful fern leaf or " star " appears upon the surface of antimony, and according to the length and form of this " star " on the ingot its quality is decided. Although the " star " is accepted as a criterion of the purity of the metal, it is really only a rough guide. It is no guarantee that the metal is more than 99% pure, as it may be produced with inferior metal, while the very best metal may show an imperfect star or none at all if not properly cast. It is this peculiar characteristic of pure antimony to crystallise on the ingot in the fern-leaf or star form when cooling which originates the trade term of "star antimony" for good quality of antimony.

Antimony may also be purified by bubbling chlorine gas through the molten metal in a manner similar to that used in the refining of gold (U.S.P. 1662439). Antimonial lead and lead-tin alloys may be freed from arsenic by blowing a current of air through the molten metal, under a layer of sodium hydroxide at 450°, whereby the arsenic is converted into sodium arsenate (B.P. 288939).

For pharmaceutical purposes it is important to prepare antimony quite free from arsenic. This may be accomplished by Wöhler's method. A mixture of 4 parts powdered commercial antimony, 5 parts sodium nitrate, and 2 parts sodium carbonate (to prevent the formation of insoluble antimony arsenate) is thrown into a red-hot crucible. Combustion takes place quietly; the mass is pressed together and more strongly heated for half an hour, so as to become pasty without fusion, being pressed down as it rises from evolution of gas. While still hot and soft it is removed, reduced to powder, and boiled with frequent stirring in water, the finer powder is poured off with the water, and the residue again treated, the washings being mixed with that first obtained. The water, which contains the whole of the arsenic but no antimony (Meyer), is removed from the insoluble portion by subsidence, decantation and filtration. The residue of sodium antimonate should be white, but the presence of lead imparts a yellow colour. It is dried and fused with half its weight of cream of tartar at a moderate heat, cooled, broken into small lumps, and the potassium and sodium salts removed by digestion in water. The powdered metal is then fused into a button.

This method may be used quantitatively for the separation of antimony from arsenic. If the sodium nitrate be replaced by potassium nitrate, a portion of the antimony will enter into solution with the arsenic as potassium antimonate (C. Meyer, Annalen, 1848, **66**, 236). Arsenic may also be completely removed by fusing the antimony in succession with first, potassium carbonate; second, potassium nitrate; third, antimonic oxide; fourth, potassium carbonate (T. Martius, Kastner's Arch. 1832, **24**, 253); or by fusing three times with fresh portions of sodium or potassium nitrate.

Pure antimony may be obtained by heating tartar emetic to low redness and digesting the resultant mass in water to remove the potassium carbonate. The powder thus obtained may be then dried and fused into a button.

Groschuff (Z. anorg. Chem. 1918, **103**, 164) describes the following method of preparing chemically pure antimony. Antimony trichloride or pentachloride is purified by distillation and converted into chloroantimonic acid, by dissolving in concentrated hydrochloric acid, passing in chlorine until the solution becomes greenish-yellow, and then introducing hydrogen chloride. After purification by recrystallisation the chloroantimonic acid is hydrolysed to antimonic acid, which is reduced to metal by fusion with potassium cyanide.

TESTS FOR IMPURITIES IN ANTIMONY.

Sulphur.—The powdered metal evolves sulphuretted hydrogen gas (which blackens lead paper) on heating with strong hydrochloric acid.

Arsenic.—If deflagrated with ¼ its weight of sodium nitrate, boiled with water, and filtered, the arsenic enters into solution, leaving the antimony behind; the solution is saturated with sulphuretted hydrogen (if an orange precipitate, consisting of antimony sulphide, falls, this must be filtered quickly; it is due to the presence of a trace of antimony in the solution). The arsenic is deposited as the lemon-yellow sulphide on standing.

Lead and Copper.—The metal is powdered and treated with dilute nitric acid, evaporated nearly to dryness, taken up with water, and filtered; the addition of sulphuric acid precipitates white lead sulphate, and the addition to the filtrate of potassium ferrocyanide gives a brown precipitate in presence of copper.

If sulphur as well as lead be present in the antimony, the lead is converted at once into sulphate by the action of nitric acid; the residue on evaporation is digested with yellow ammonium sulphide, which dissolves the antimonic oxide and leaves black lead sulphide.

Iron.—The powdered metal is ignited with three parts nitre and washed with boiling water; the residue is boiled with hot dilute hydrochloric acid; on the addition of potassium ferrocyanide a blue precipitate is produced.

Detection of Antimony.—When fused on charcoal with potassium cyanide or sodium carbonate or a mixture of the two, antimonial compounds produce a brittle bright bead of metallic antimony with white fumes and a white incrustation on the charcoal; the bead leaves a white residue on treatment with nitric acid, which is soluble in cream of tartar or tartaric acid. A delicate confirmatory test, given by Crookes, is to add to the white incrustation on the charcoal one drop of ammonium sulphide, when the formation of the orange sulphide is conclusive evidence of the presence of antimony. Sulphide of antimony melts readily in the candle flame.

Estimation of Antimony.—*See* CHEMICAL ANALYSIS.

PROPERTIES OF ANTIMONY.

Physical.—Antimony is a lustrous, bluish-white metal, which has a coarsely laminated or granular structure, according as it has been slowly or quickly cooled. Ordinary metallic antimony crystallises in rhombohedral or trigonal crystals.

The sp.gr. of the metal is 6·72–6·86. It melts at 630°C., and boils at about 1635°C. in a current of hydrogen. Antimony has a hardness of 3–3·5, and is so brittle that it can readily be powdered. It is a bad conductor of heat, being 4·02 as compared with silver **100**, and also a bad conductor of electricity, being 4 as compared with silver 100. The most important physical property of antimony is that of expanding on solidification, a property possessed also by its alloys.

The element occurs in three modifications: (1) the crystalline or ordinary form described above; (2) yellow modification, soluble in carbon disulphide, which is produced by the action of oxygen on liquid stibine at −90°; and (3) the amorphous explosive antimony, which is best prepared by the action of a weak constant electric current on a concentrated acid solution of antimony trichloride, the strength of current bearing a constant relation to the surface of deposition, not less than ½ grain being deposited per sq. in. per hour. Thus produced, it is bright and steel-like in appearance, with an amorphous fracture and sp.gr. 5·78. When heated to 200°, or struck or scratched, it rapidly changes into the crystalline form, increasing in density, with the production of great heat. Antimony trichloride is always contained in the metal to the extent of 4·8–7·9%, and is given off when the form changes. It is probable that this substance is a solid solution of an antimony halogen compound in an allotropic form of antimony, and that the explosion consists in the rapid transformation of the latter into the stable form. The change is accompanied by an evolution of heat amounting to 20 cals. per g. Cohen and others (Z. physikal. Chem. 1904, **47**, 1; 1905, **50**, 291; 1905, **52**, 129) have shown that this change goes on slowly when explosive antimony is preserved.

Explosive antimony is shown by X-ray analysis to be amorphous before exploding and crystalline afterwards (H. Kersten, Physics, 1932, **2**, 276).

Explosive antimony prepared by electrodeposition is shown by electron-diffraction analysis to be identical with the amorphous films produced by distillation in a high vacuum. When such an amorphous film is heated to 120°–150° crystallisation occurs. The amorphous form is considered to be in the supercooled liquid state (J. A. Prins, Nature, 1935, **136**, 299).

Chemical.—At the ordinary temperature antimony is not acted on by the air, but oxidises quickly on melting, and burns at a red heat, producing white fumes of the trioxide. It is oxidised by nitric acid of various strengths, dilute acid producing principally the trioxide, and the concentrated acid producing the pentoxide. Dilute sulphuric and hydrochloric acids are without action on it, but the strong acids produce the sulphate and chloride respectively. When fused with borax or other vitrifying material, it imparts to them a yellow colour.

Antimony combines directly with the halogens with evolution of light and heat, and also, at a higher temperature, with the elements of the sulphur group, and with phosphorus and arsenic.

Antimony is precipitated as a fine powder by the action of zinc on an acid solution of an antimony salt. In this form it is sold as "iron black" for producing an appearance of polished steel on papier maché, plaster of Paris, and zinc ornaments.

Brass can be covered with a fine lustrous coating of antimony by dipping in a hot solution of 1 part tartar emetic, 1 part tartaric acid, 3 or 4 parts powdered antimony, 3 or 4 parts hydrochloric acid, and 3 parts water.

Antimony may be deposited electrolytically on brass or copper by using a bath of the double chloride of antimony and ammonium acidified with hydrochloric acid.

ALLOYS OF ANTIMONY.

Antimony alloys with most of the heavy metals and with the alkali metals. It dissolves in a solution of sodium in liquid ammonia. It generally increases the fusibility, brittleness, and hardness of the metals with which it is alloyed, and imparts the valuable property of expanding on solidification, thus producing very fine impressions. The sharpest impressions are produced when any of these alloys are cast at a low temperature (J.S.C.I., 1882, **1**, 982). The castings are usually made in brass moulds coated with lampblack and turpentine.

With *lead*, antimony alloys readily in all proportions. An alloy of equal parts of lead and antimony is very brittle, and rings when struck. Nasmyth has recommended the addition of 5% antimony to lead for use instead of bronze in taking casts of works of art (Athenæum, No. 1176, 511).

Type metal is essentially an alloy of lead and antimony, frequently with addition of tin and containing less frequently copper. A few examples of common type metals are:

	Lead.	Antimony.	Tin.	Copper.
Type metal . .	55	30	15	—
,, . .	70	18	10	2
,, . .	77·5	16	6·5	—
,, . .	82	15	3	—
Stereotype plate	85·7	14·3	—	—
,, ,,	82·5	13	4·5	—
Linotype metal .	84·5	13·5	2	—
,, ,,	83	12	5	—

The alloys, containing varying proportions of antimony, are also used, under the name of *hard lead*, in lead pipes, for making pumps and taps for raising acid in alkali works, in the manufacture of shrapnel and shot, for battery plates, toys, cable covering, siphon taps, and for the emery wheels and tools of the lapidary.

Tin forms numerous useful alloys with antimony, especially with the addition of other metals. *Common Britannia metal* contains tin 94, copper 1, antimony 5. Britannia metal for casting: tin 90·6, copper 0·2, antimony 9·2. The best Britannia metal contains tin 90, antimony 10, lead and bismuth being carefully excluded. Copper is never added except for the production of colour. Increasing the proportion of antimony raises the m.p., increases the hardness, and decreases the malleability of the alloy. Good alloys take a brilliant polish, and show a fine-grained, jagged fracture. The presence of arsenic in the antimony diminishes the ductility of the product.

Metal argentum contains tin 85·5, antimony 14·5.

Ashbury metal: tin 77·8, zinc 2·8, antimony 19·4.

Ships' nails: tin 50, lead 33, antimony 17.

Minofer is tin 68·5, antimony 18·2, copper 3·3, and zinc 10.

Bearing or *anti-friction metal* usually contains antimony, tin, lead and copper, but the composition is very variable. As the name indicates, it is used for machinery bearings, being especially suitable for light loads at high speeds. As examples of these alloys the following may be given :

	Antimony.	Tin.	Copper.	Lead.
Babbitt metal .	8·3	83·3	8·3	—
Railway bearings	15	8	2	75
,, ,, .	13·5	11·5	3	72
,, ,, .	10	51	2	37
U.S. Rly. Babbitt metal . .	7·4	88·9	3·7	—
German Rly. Babbitt metal .	6·1	88·3	5·6	—

Copper.—The presence of 0·15% of antimony renders copper both cold and hot short. With varying proportions of the two metals shades from pure copper-red to rose-red, crimson, and violet may be obtained, the last when equal parts of each are present. Two definite compounds of copper and antimony appear to exist, viz. $SbCu_2$, a violet alloy known as *Regulus of Venus*, and $SbCu_3$, which has a close-packed hexagonal structure.

Antimony is sometimes added to brass to heighten its colour. These alloys are harder and finer in texture than copper or brass, they take a better polish, and are sometimes used for concave mirrors.

Zinc.—Antimony forms alloys with zinc which decompose water rapidly at the boiling temperature, and this action is promoted by the presence of traces of platinic chloride. Cooke has suggested the suitability of this reaction for the preparation of pure hydrogen.

Melted gold absorbs the vapour of antimony, but gives it up almost entirely on further heating. Gold loses its malleability when $\frac{1}{2000}$ of antimony is present. An alloy of 9 gold and 1 antimony is white and very brittle, with an amorphous porcelain-like fracture. Silver antimonide occurs as the mineral *discrasite.*

Compounds of Antimony.

The principal compounds of antimony are formed by combination with sulphur, chlorine and oxygen ; some compounds contain two of these negative elements, of which the oxychloride or *powder of Algaroth* and the oxysulphide or *glass of antimony* are examples.

The most important of these are the trisulphide, trichloride and trioxide.

Antimony trisulphide, Sb_2S_3. *Crude antimony, antimony ore, sesquisulphide of antimony ; Schwefelspiessglanz ; Grau - Spiessglanzerz ; Stibium sulphuratum nigrum ; lupus metallorum.*

This substance, as it occurs naturally, or after liquation, is usually too impure to be employed for other purposes than the preparation of the metal.

Small quantities of the liquated sulphide are used in the primers of shells and also in the charge of some shells to produce on explosion a white smoke which is of service in range-finding.

The ordinary sulphide may be prepared by the following methods :

(1) Thirteen parts pure antimony are mixed with 5 parts flowers of sulphur, and projected in portions into a red-hot crucible ; when completely fused it is poured out and any free metal detached.

(2) Sulphuretted hydrogen precipitates it as an orange precipitate from a solution of an antimony salt.

(3) One part crude antimony sulphide, 1 part pearl ash, 1½ parts lime, and 15 parts water are digested for two hours in a closed vessel and sulphuric acid is added ; the alkaline sulpho-salt first formed is decomposed by the acid with the precipitation of the pure sulphide.

Antimony sulphide is soluble in alkaline sulphides and in acid potassium sulphate. When finely powdered and rubbed to a paste at 20° or 30° with strong sodium sulphide solution, a coppery metallic mass is produced, and the liquor, on addition of more sodium sulphide, yields *Schlippe's salt* (*v. infra*).

The sulphide is used to some extent in the preparation of safety matches and percussion pellets for cartridges, in pyrotechny and in veterinary surgery.

Kermes mineral. *Brown-red antimony sulphide. Pulvis Carthusianorum. Sulph. stibiatum rubrum.*

Kermes mineral usually consists of a mixture of the trisulphide and trioxide containing alkali. Berzelius and Rose state that some samples examined by them consisted of a true double sulphide of potash and antimony.

Preparation.—The following methods may be used :

(1) Four parts pure potassium carbonate and 11 parts pure antimony sulphide are heated to fusion in a covered crucible, cooled, boiled with water and filtered. The solution on exposure to the air deposits kermes ; the residue from the first boiling is heated with the mother liquor from some previously deposited kermes, and yields a further quantity ; this operation is repeated until an insoluble residue of trisulphide and trioxide is left. Each successive deposit of the kermes contains a larger amount of the oxide.

(2) Two parts antimony, 1 sulphur and 3 sodium carbonate, or 1 antimony sulphide and 3 or 4 tartaric acid, are fused together until fumes cease to be evolved ; and the product is treated as in (1).

(3) The slags from the reduction of antimony ore with cream of tartar slowly precipitate kermes when treated with water ; this is sold to veterinary surgeons as "kermes by the dry way." When antimony sulphide is boiled with potash and precipitated with an acid, the kermes produced contains no oxide (Liebig). The kermes produced by the action of *dilute* alkaline carbonate on antimony sulphide also contains no oxide (Rose). The oxide may be removed from ordinary kermes by digestion with tartaric acid. A solution containing so much alkali as to give no precipitate on cooling gives, when treated with carbon dioxide, a highly sulphurated kermes containing antimony pentasulphide.

Kermes is a brown-red, loosely coherent powder, with a brown streak, containing water, which is given off below 100°. It is lighter than the ordinary sulphide. The kermes containing antimony oxide, when fused and solidified, is destitute of crystalline structure, while that free from oxide produces a highly crystalline solid.

Antimony pentasulphide, Sb_2S_5. *Golden sulphide of antimony ; sulphur antimonii auratum.* Prepared by boiling the trisulphide with potash and ground sulphur, filtering and precipitating with acid. Redwood recommends 4 parts black antimony sulphide, 8 lime, and 80 water, digested, filtered and precipitated with hydrochloric acid ; or 2 sulphide, 4 potassium carbonate, and 1 sulphur, fused, treated with 20 parts water, filtered, and the solution precipitated with a large excess of sulphuric acid. The preparation is also covered by U.S.P. 1633754 and 1671203.

On treating the mother liquor from kermes mineral with an acid, the pentasulphide is precipitated with evolution of sulphuretted hydrogen. *See* F.P. 605401.

Antimony pentasulphide is of some importance commercially as it is used in the process of vulcanising rubber, also in colouring red rubber and as a paint pigment.

Antimony pentasulphide combines with alkaline sulphides, forming sulphantimonates, which as well as the sulphantimonites (derived from H_3SbS_3) are known as "livers of antimony." Of these the sodium sulphantimonate,

$$Na_3SbS_4,9H_2O,$$

or *Schlippe's salt*, is the most important. For the preparation of this salt a mixture of 11 parts finely powdered antimony trisulphide, 13 crystallised sodium carbonate, 1 flowers of sulphur, 5 recently slaked lime, and 20 water is digested at the ordinary temperature for 24 hours with frequent stirring, in a vessel which can be closed. It is then strained and washed several times with water ; the solution and washings are evaporated in a porcelain or clean iron dish until a sample yields crystals on cooling ; the solution is then cooled and the resultant crystals washed with cold water and dried in the open air or in a desiccator at the ordinary temperature. The salt is more rapidly formed when the mixture is heated. (*See also* A. Sartorius, Apoth.-Ztg. 1908, **23**, 342.)

Oxysulphides of antimony are formed by the combination of the sulphides and oxides or by the partial oxidation of the sulphides.

Antimony crocus or saffron of antimony.—Three parts of antimony trioxide and 1 part trisulphide, or the oxide with the calculated quantity of sulphur, are fused together.

The scoria from the fusion of the sulphide with carbon and alkaline carbonate in the preparation of the metal is also known as *crocus of antimony*, which is a brownish-yellow body.

Glass of antimony. Vitrum antimonii, is formed when antimony sulphide is fused until the necessary amount of sulphide has been converted into oxide and the whole forms a glassy mass. The best method of preparation is to roast the sulphide completely into oxide and fuse the product with $\frac{1}{20}$ part of sulphur. Its colour varies with the proportion of sulphur present from yellowish-red to hyacinth red. The best quality is of a fine red colour, and contains 8 antimonious oxide and 1 antimonious sulphide.

Antimony cinnabar is an oxysulphide of a fine vermilion colour, soft and velvety, and unaltered by air or light ; it is used in the preparation of oil and water colours, and in calico-printing. It is prepared by dissolving antimony oxide in hydrochloric acid, and placing the solution in a large wooden tub which is $\frac{7}{8}$ filled with calcium thiosulphate. The mixture is stirred and heated with steam to 70° ; the precipitate soon subsides as a yellowish sediment which changes to a bright orange-red, and is thoroughly washed, and dried below 50°.

Antimony yellow (*Mérimée's yellow*). According to the method of Mérimée, a mixture of 3 parts bismuth, 24 parts antimony sulphide, and 64 parts nitre, is thrown little by little into a heated crucible, fused, powdered, washed and dried. In this way bismuth antimonate is produced. Of this 1 part is mixed with 8 parts ammonium chloride and 128 parts litharge, and fused as before. The time occupied and the temperature used cause considerable variations in the colour. Mérimée's yellow is a fine permanent colour of good body. It is used for the finest painting and in the ceramic industries.

Naples yellow is essentially an antimonate of lead containing excess of lead oxide, but mixtures of carbonate and chromate of lead are also sold under the name. Many processes may be used for its preparation. According to Brunner, a mixture of 1 part tartar emetic, 2 parts lead nitrate, and 4 parts sodium chloride is heated just to fusion, for 2 hours. The cooled mass is placed in water and soon falls to pieces. According to Guimet, it may be produced by heating a mixture of 1 part potassium antimonate and 2 parts red lead. It is a fine, very permanent orange or yellow pigment, used in oil-painting, and, mixed usually with a lead glass, for glass and porcelain staining.

Antimony trichloride. *Butter of antimony.*—Prepared by dissolving the sulphide in strong hydrochloric acid with a small quantity of nitric acid and evaporating to dryness.

To prepare the pure chloride, the acid solution is evaporated until it just crystallises on standing in a cool place ; it is then transferred to a retort and distilled until a drop of the distillate solidifies on a cold surface ; the receiver is then changed, and the further distillate is pure.

It is a white, buttery, semivitreous, deliquescent solid. When pure, it is crystalline, and melts sharply at 73·2°, and boils at 223·5° (Beckmann, Z. anorg. Chem. 1906, **51**, 96). It is used as a caustic in medicine, for the preparation of tartar emetic, and as a "bronzing solution" for gun-barrels, etc. For this purpose a saturated solution is mixed with olive oil, rubbed over the warmed metal, and exposed to the air until the proper colour is produced. When bronzed, the metal is polished with a burnisher or with wax, or coated with a varnish of 2 oz. shellac, 3 drachms dragon's blood, dissolved in 2 quarts of methylated spirit.

Antimony oxychloride. *Basic chloride, powder of Algaroth; pulvis Algarothi; pulvis angelicus; mercurius vitæ, etc.*

Water is added to a solution of the trichloride until it is distinctly turbid, when it is filtered (the precipitate carries down any traces of sulphuretted hydrogen which may be present, and which if left would soon turn the substance yellow). Five to ten volumes of water are added, and the precipitate is washed with cold water and filtered. Its composition varies with the temperature at which it is produced and the amount of water used, varying between $SbOCl$ and, where a very large amount of water has been used, Sb_2O_3. It is a white powder, and is principally used for the preparation of pure antimonious oxide and tartar emetic, and has been used as a pigment.

Antimonious oxide, Sb_4O_6. *Trioxide of antimony.* If antimony is powdered and heated in a shallow dish, it eventually forms antimony tetroxide, Sb_2O_4; this, together with the unchanged metal, is fused in a crucible, when the tetroxide and antimony react, forming antimonious oxide, the excess of antimony sinking to the bottom of the crucible.

For pharmaceutical purposes 20 parts of finely powdered antimony sulphide are gradually added to 100 parts hydrochloric acid containing 1 part nitric acid and heated, gently at first, and then more strongly, until sulphuretted hydrogen ceases to be evolved. It is then boiled for an hour, enough water is added to produce a slight precipitate, which removes the last traces of sulphuretted hydrogen, and filtered into a vessel containing water, precipitating the oxychloride, which is filtered and washed until it ceases to have an acid reaction; it has then become converted into the trioxide.

It is a white fusible solid, melting-point 656°C., slightly soluble in water, volatile at 1,570°C. It becomes further oxidised to the non-volatile tetroxide, Sb_2O_4, on heating in air.

It is used for the preparation of tartar emetic. When ground with linseed oil it is sometimes used as a substitute for white lead, being less injurious to the workmen and less acted upon by sulphur gases; it has, however, less "body" and is more expensive.

Tartar emetic. *Potassium antimony tartrate. Tartarus stibiatus. Brechweinstein; Spiessglanzweinstein.* $2C_4H_4K(SbO)O_6,H_2O$. Three parts antimonious oxide and 4 of cream of tartar are made into a thin paste with water and digested for about half an hour, keeping the water at constant volume; 8 parts of water are then added, boiled, and filtered whilst hot. The oxychloride or oxysulphide may be substituted for the oxide, but not so satisfactorily.

Tartar emetic forms octahedral crystals, which give off a part of their water on exposure to the air. They dissolve in 14·5 parts cold and in 1·9 parts boiling water. They show an acid reaction with litmus and have a nauseous metallic taste, 5–10 centigrams causing vomiting, and larger quantities being very poisonous.

It is used in medicine and in the preparation of pomades, etc., and also largely as a mordant in dyeing and calico-printing. Mixtures of tartar emetic for mordanting are sold containing as much as 33–59% zinc sulphate at a lower price, under the names *tartar emetic powder, tartar emetic substitute, antimony mordant, etc.* It is known that zinc acetate may partly replace the tartar emetic with advantage, but the sulphate appears to be a simple adulterant (H. Smid, Chem.-Ztg. 1882, **6**, 949).

Several other compounds of antimony have been proposed for mordants instead of tartar emetic. E. Jacquet (Dingl. poly. J. 1885, **257**, 168) advised the use of a mixture of basic antimony oxalate with twice its weight of ammonium oxalate. Nölting recommended the double oxalate of potash or of ammonia and antimony (Dingl. poly. J. 1884, **255**, 122). It is stated that the latter compounds have long been used under other names.

Antimony trifluoride, SbF_3, is obtained as a dense snow-white mass by distilling antimony with mercury fluoride. It may also be obtained in rhombic pyramids by the evaporation of a solution of the oxide in hydrofluoric acid. It is deliquescent and is not decomposed by water, but if the solution be evaporated without an excess of hydrofluoric acid a basic fluoride is formed.

The use of the trifluoride (which is not precipitated with excess of water) and the double fluorides of antimony and the alkalis has been patented by S. M'Lean. G. Watson (J.S.C.I. 1886, **5**, 591) patented a process for using trichloride with sufficient common salt to prevent the precipitation of the oxychloride. A double salt of antimony fluoride and ammonium sulphate, $SbF_3(NH_4)_2SO_4$, known as "antimony salts," is also used in dyeing, but as it attacks glass as well as metal, it should be stored and worked in wooden vessels. A good bath is 100 litres water, 400 g. antimony salts, 200 g. soda crystals, at a temperature of 50° (Frey, Bull. Soc. Ind. Mulhouse, 1888, 301).

Antimony pentafluoride, SbF_5, is obtained by the action of anhydrous hydrofluoric acid on antimony pentachloride (Ruff and Plato, Ber. 1904, **37**, 673; 1906, **39**, 4310; 1909, **42**, 4021). It combines with antimony trifluoride with evolution of heat. It forms difficultly crystallisable double salts with the fluorides of the alkali metals.

C. O. B.

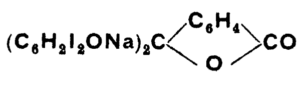
ANTIMONY CACODYL *v.* ANTIMONIALS, ORGANIC.

ANTIMONY CROCUS or SAFFRON *v.* ANTIMONY.

"ANTIMONY SALT" *v.* ANTIMONY; TARTAR EMETIC.

ANTINONIN. Trade name for a solution of potassium *O*-dinitrocresol, used as a fungicide.

ANTINOSIN. Trade name for the sodium salt of tetra-iodophenolphthalein (*nosophen*),



$$(C_6H_2I_2ONa)_2C\left\langle\begin{matrix}C_6H_4\\O\end{matrix}\right\rangle CO$$

Antiseptic, also used for skiagraphy (X-ray diagnosis).

ANTIPERIODYIN, ANTIPERIOSTIN. Trade names for mercury iodocantharidate.

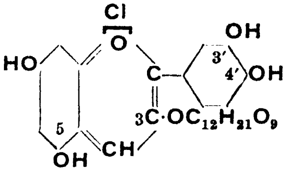
ANTIPYRIN, *phenazone.* 1-Phenyl-2:3-dimethyl-5-pyrazolone, $C_{11}H_{12}ON_2$, m.p. 111°–113°. Antipyretic and analgesic.

ANTIRRHINIC ACID *v.* DIGITALIS.

ANTIRRHININ. The anthocyanin pigment of the magenta and crimson *Antirrhinum majus* was isolated as a hydrochloride,

$$C_{27}H_{31}O_{15}Cl,$$

from the latter variety by Scott-Moncrieff (Biochem. J. 1930, **24**, 753). Four distinct hydrates were obtained differing in colour, crystalline form, and solubility. It is a 3-rhamnoglucoside of the 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride *cyanidin,*



and is probably identical with *keracyanin* and *prunicyanin* previously isolated from cherries and plums respectively by Willstätter and Zollinger (Annalen, 1916, **412**, 164) and certainly identical with the flower pigment of two varieties of flowering currant, *Ribes sanguineum*, recently obtained by Nolan and Brady (Proc. Roy. Irish Acad. 1936, **43B**, 1), with which it has been compared.

The colour reactions of *antirrhinin* are those typical of a 3-glycoside of cyanidin with free hydroxyl groups at 3′ and 4′, *i.e.* sodium acetate gives a violet-red, sodium carbonate blue-violet, caustic soda pure blue and ferric chloride a deep violet. The "distribution number" or specific partition value between amyl alcohol and 0·5% aqueous HCl is comparatively high (8) in concentrated (0·02%) extracts, but falls nearly to zero on dilution with aqueous acid (distinction between pentose glycoside and monoglycoside: Robinson and Robinson, Biochem. J. 1932, **26**, 1650). Antirrhinin picrate is freely soluble in aqueous picric acid.

The relative positions of the rhamnose and glucose residues, which are both situated at position 3, have been elucidated by means of a partial hydrolysis with cold concentrated HCl whereby the rhamnose was detached from the glucose, leaving a 3-monoglucoside of cyanidin (Scott-Moncrieff, unpublished). Complete hydrolysis of antirrhinin yielded cyanidin (1 mol.), glucose (1 mol.), and rhamnose (1 mol.).

The dominance of the cyanidin type of pigmentation of magenta and crimson flowers of *Antirrhinum* over the paler and less oxidised pelargonidin pigmentation of the pink and bronze forms follows the general rule observed in flower colour variation (Onslow, Nature, 1932, **128**, 373; Scott-Moncrieff, J. Genetics, 1936, **32**, 117).

If an ivory flower pigmented by the flavone *apigenin* is crossed with a white of certain genetical constitution a magenta type containing both *antirrhinin* and *apigenin* is obtained. The lack of a simple chemical relationship between these pigments does not support the theory of Everest (Proc. Roy. Soc. B, 1918, **90**, 251) that the anthocyanins are formed directly from the flavones. Since increase in one of these pigments is accompanied by decrease in the other, it is suggested that they are formed by parallel syntheses from a limited common precursor. R. S.-M.

ANTISEPTICS *v.* DISINFECTANTS.

ANTITUSSIN. Difluorodiphenyl,

$$FC_6H_4{\cdot}C_6H_4F,$$

m.p. 87°. Used in dermal treatment.

ANTIVENIN *v.* SNAKE VENOM.

ANTODYNE. Trade name for α-glyceryl phenyl ether, phenoxy-dihydroxy-propane,

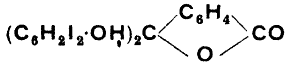
$$C_6H_5O{\cdot}CH_2{\cdot}CH(OH)CH_2{\cdot}OH,$$

m.p. 69°. Hypnotic.

ANTOX. *Antimony White. Timonox.* Trade name for antimonious oxide, Sb_2O_3, used as a pigment.

ANTWERP BLUE. Prussian Blue of a characteristic shade.

APALLAGIN. Trade name for the mercury salt of tetraiodophenolphthalein,



$$(C_6H_2I_2{\cdot}OH)_2C\left\langle\begin{matrix}C_6H_4\\ O\end{matrix}\right\rangle CO$$

APATITE. A crystallised mineral, consisting of calcium phosphate in combination with fluorine, chlorine, hydroxyl, or carbonic acid, the formula being $(CaF)Ca_4(PO_4)_3$ or $3Ca_3(PO_4)_2+CaF_2$, where F may be replaced by Cl, OH, or CO_3. There are thus several chemical varieties, namely, fluor-apatite, chlor-apatite, hydroxy-apatite, carb-apatite and oxy-apatite; the last two being also called podolite $(3Ca_3(PO_4)_2,CaCO_3)$ (V. N. Chirvinsky, 1907) and voelckerite $(3Ca_3(PO_4)_2,CaO)$ (A. F. Rogers, 1912) respectively. Similarly, by partial replacement of the calcium, there are the chemical varieties mangan-apatite, cupro-apatite and talc-apatite. In addition to these, some other trivial names are applied to varieties of crystallised apatite; for example, asparagus-stone, from Murica in Spain; moroxite, from Arendal in Norway; and francolite, from Wheal Franco, near Tavistock in Devonshire. The distinction between fluor-apatite and chlor-apatite is, however, the only one of any importance. (For the varieties of massive apatite, *v.* PHOSPHORITE.)

Apatite is often found as well-developed crystals. These belong to the hexagonal system, and are usually bounded by a six-sided prism and pyramid with the basal plane, though sometimes numerous other brilliant facets are present. The colour is commonly greenish or brownish, but sometimes sky-blue, violet or colourless. The crystals may be transparent or opaque, and they have a vitreous to sub-resinous lustre. Sp.gr. 3·2; hardness 5 (the mineral can be scratched with a knife). Owing to its variable appearance, apatite is frequently mistaken for other minerals, and it well deserves its name, from ἀπατάω, "to deceive." In determining the mineral, it is always well to test for phosphoric acid.

As microscopic crystals, apatite is present as an accessory constituent of igneous rocks of all kinds. It also occurs in metamorphic rocks and in metalliferous veins. Fine specimens are found at many localities, but only in two regions—in Norway and Canada—is crystallised apatite mined for commercial purposes. In southern Norway, particularly in the neighbourhood of Kragerö and Oedegaarden, near Bamle, extensive deposits of chlor-apatite occur in connection with gabbro (a pyroxene-felspar-rock of igneous origin). Large deposits of fluor-apatite are mined in Ottawa Co., Quebec, and in Renfrew Co., Ontario; here the mineral forms beds in Laurentian gneiss, usually in association with crystalline limestone. In the iron mines at Mineville, in Essex Co., New York, small grains of apatite occur disseminated in magnetite, sometimes to the extent of 5% of the mass. Here it is separated by a magnetic process, and used for the manufacture of fertilisers.

Large deposits of crystallised apatite were discovered in 1925–27 to the east of the Murmansk railway in the Kola peninsula in Arctic Russia. A sheet 45–60 metres thick extends for several kilometres across the hills Kukisvumchorr, Yukspor, Rasvumchorr, and Poachvumchorr, and sixty million tons of "ore" containing 60–80% of apatite are in sight. At the new town of Khibinogorsk[1] 400,000 tons of apatite were produced in 1931, being separated by flotation from the "ore." The sheet of "ore" is a coarse-grained aggregate of apatite 85% and nepheline and ægirine 10–15%, with small amounts of sphene, titanomagnetite, eudialyte, eucolite, ænigmatite, astrophyllite, etc.; and it penetrates along veins into the overlying nepheline-syenite and the underlying urtite. It represents the residual magma of the urtite intrusion. The apatite is white to pale yellow or green, and contains fluorine and cerium. The associated nepheline is used in the ceramic industry and as a source of potassium and aluminium (A. E. Fersman, "The apatite-nepheline problem of the Khibinsky tundra," Materials for chemicalizing natural economy U.S.S.R. (Russ.), Leningrad, 1929, no. 5 (*see* Min. Mag., March 1936, Abstr. **6**, 232, 312, 366). B. Granigg, Z. prakt. Geol. 1933, **41**, 1, 25; L. B. Antonov, "The apatite deposits of Khibina tundra," Khibina Apatite, Leningrad, 1934, **7** [Min. Mag. 1936, Abstr. **6**, 232, 312, 366]).

On the Norwegian deposits, *see* J. H. L. Vogt, Die Apatit-Ganggruppe, Z. prakt. Geol. 1895, **3**, 367, 444, 465. On the Canadian deposits, the various publications of the Canadian Geological Survey. *See also* O. Stutzer, "Die wichtigsten Lagerstätten der 'Nicht-Erze,'" Berlin, 1932, vol. 4. L. J. S.

APHTHITALITE. Native sulphate of potassium and sodium, $(K,Na)_2SO_4$, containing $K : Na$ in ratios varying from 3 : 1 to 4 : 3. It occurs sparingly as crusts and delicate platy crystallisations on Vesuvian lava; these are colourless, or often tinged with blue or green. The crystals are rhombohedral and optically uniaxial, although often simulating orthorhombic forms; and are dimorphous with the usual orthorhombic modification of potassium sulphate obtained artificially. The same mineral has been found at Rocalmuto, Sicily, in the potash-salt deposits at Douglashall, near Westeregeln, in Prussia, and in the salt mine at Stebnik in Poland. Synonyms are arcanite and glaserite. L. J. S.

APHYLLINE, APHYLLIDINE *v.* SPARTEINE.

A.P.I. American Petroleum Institute gravity scale:

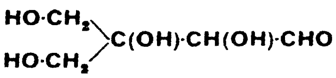
$$\text{degrees A.P.I.} = \frac{141{\cdot}5}{\text{sp.gr. at } 60°\text{F.}} - 131{\cdot}5.$$

High values in degrees A.P.I. correspond to low specific gravities.

APIGENIN *v.* FLAVONE.

APIIN, $C_{26}H_{28}O_{14}$, m.p. 228°, $[\alpha] -130°$; the glycoside present in the leaves and seeds of parsley is hydrolysed to glucose, apiose (*q.v.*) which is an abnormal branched chain C_5 sugar and apigenin 5 : 7 : 4′-trihydroxyflavone. The attachment of the glucose is through the 7-hydroxyl group. Apiin is not hydrolysed by the α- or β-sucroclastic enzymes. E. F. A.

APIOSE, $C_5H_{10}O_5$, the sugar of the flavone glycoside apiin, which is found in parsley, contains a branched chain of carbon atoms:

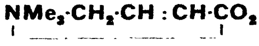


$$\begin{matrix} HO{\cdot}CH_2 \searrow \\ \quad C(OH){\cdot}CH(OH){\cdot}CHO \\ HO{\cdot}CH_2 \nearrow \end{matrix}$$

The glycoside contains the disaccharide glucoapiose, from which apiose is split off by the action of dilute mineral acids (Vongerichten, Annalen, 1901, **318**, 121; 1902, **321**, 71; Ber. 1906, **39**, 235; Schmidt, Ann. 1930, **483**, 115). It is a pale yellow syrup, optically inactive, nonfermentable, does not yield furfurol, is oxidised by iodine and barium hydroxide to apionic acid, which yields *iso*valeric acid when reduced by hydrogen iodide and phosphorus. The phenylhydrazone has m.p. 135°; phenylosazone, m.p. 156°; and the bromophenylosazone, m.p. 209°–212°. E. F. A.

APIUM PETROSELINUM (*Carum petroselinum*) *v.* PARSLEY.

APOCARNITINE, CROTONBETAINE. γ-Dimethylaminocrotonic methyl betaine,



$$NMe_3{\cdot}CH_2{\cdot}CH:CH{\cdot}CO_2$$

from carnitine (in ox muscle) (A. 1928, 665) by loss of H_2O. Synthesis by Linneweh (Z. physiol. Chem. 1928, **176**, 217; A. 1928, 1122).

APOLLO RED *v.* DYESTUFFS, Azo.

APOLYSIN. Trade name for the monophenetidine derivative of citric acid,

$$EtO{\cdot}C_6H_4{\cdot}NH(C_6H_7O_6),$$

m.p. 72°. Antipyretic.

APOMORPHINE *v.* OPIUM.

APONAL. Trade name for amyl carbamate, $NH_2{\cdot}CO{\cdot}OCMe_2Et$. Hypnotic.

APOREINE. A poisonous alkaloid found in the juice of *Papaver dubium*, m.p. 88°–89°.

---

[1] Since renamed Kirovsk.

Forms crystalline salts, giving a bluish fluorescence in solution. The hydrochloride,

$$C_{18}H_{16}NO_2,HCl,$$

forms silvery nacreous scales, subliming without decomposition in dry carbon dioxide between 220° and 240°. The neutral (normal) sulphate melts at 70°–75°, and when exposed to air and light decomposes, forming a reddish-brown powder (Pavesi, Gazzetta, 1914, **44**, 398). G. B.

APORPHINE ALKALOIDS *v.* Isoquinoline Alkaloids.

APOTHESINE. Trade name for γ-diethylaminopropyl cinnamate hydrochloride,

$$PhCH:CH{\cdot}CO{\cdot}OCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2,HCl,$$

m.p. 136°. Local anæsthetic.

APPLE, *Pyrus Malus* (Linn.). The estimated average consumption of culinary and dessert apples in the United Kingdom over the period 1928–1934 was, in round figures, 500,000 tons per annum ; of this about 200,000 tons were grown in the U.K., the remaining 300,000 tons being imported. In addition the U.K. produced 50,000 tons per annum of cider apples. The estimated total number of apple trees in the U.K. in 1931 was 15,000,000.

The many varieties of cultivated apples are used for dessert, for culinary purposes, or for making cider. Certain varieties may be used for more than one of these three purposes, but most are suited for one purpose only.

Apples used for cider (*q.v.*) give juices of relatively high "tannin" content and low acidity, and a typical cider apple has a bitter-sweet flavour ; culinary varieties have a high acidity ; dessert varieties are rich in aromatic substances which impart flavour. But all three classes of varieties vary widely in composition. The composition of a given variety varies from soil to soil and according to the type of cultivation and manurial treatment.

Most apple trees are budded or grafted on a rootstock of a different variety. This rootstock consists of a root system and a main stem, which varies in length from 1 ft. in a bush tree to 6 ft. in a standard tree. The rootstock influences the scion variety "worked" on it in respect to the age at which it begins bearing, the season at which its fruit matures, rate and type of growth, resistance to insect, fungus, and nutritional diseases, and chemical composition, both of the fruit and other parts of the tree.

Apple leaves contain 1% phloridzin and 1% maloloic acid (G. Rivière, G. Pichard, Compt. rend. 1924, **179**, 775).

Apple bark also contains phloridzin (E. M. Harvey, Oregon Agric. Exp. Stat. Bull. 1925, **215**, 3.)

Quercetin was isolated from apple peel by C. E. Sando (J. Agric. Res. 1924, **28**, 1243). Power and Chesnut (Perf. and Essent. Oil Rec. 1921, **12**, 123 ; J. Amer. Chem. Soc. 1922, **12**, 2938) isolated ethereal oil (0·00098%) containing geraniol, citral, amyl esters, and a hydrocarbon.

The acids of the apple consist principally of malic acid along with a relatively large amount of citric acid, small amounts of succinic acid and lactic acid, a very small amount of oxalic acid, and traces of unsaturated acids (H. Franzen, F. Helivert, Z. physiol. Chem. 1923, **127**, 14).

Apple juice is a good source of sorbitol (F. Tutin, Biochem. J. 1925, **19**, 416).

Much work has recently been done on the storage of apples, as a result of which English apples are marketed nearly all the year round and apples from Canada, the United States of America, Australia, Tasmania, New Zealand and elsewhere are transported safely and placed on the British market. This lengthening of the normal storage life of the apple has resulted from a close study of its physiology while still on the tree, as well as after picking. During the first three weeks after petal fall the apple increases in size, as a result of *cell division*, until it is about the size of a walnut ; next follows a long period of growth by *cell enlargement*, which ends in a short stage of *maturity*, when the fruit develops aroma and flavour, becomes yellower and falls from the tree ; the apple after falling or picking continues to live as a detached organ and enters on a period of *senescence* ; during this period it is particularly prone to attack by micro-organisms, and if it escapes these it finally succumbs to functional breakdown. The *cell division* stage is characterised by rapid increases in proteins and their precursors the amino-acids ; starch is absent and there is little sugar. During *cell enlargement* the nitrogenous constituents continue to accumulate, but the stage is characterised by the accumulation of sugars, which become the principal constituents, increasing from 1% at the beginning of the stage to 9% of the fresh weight at the end. During *cell division* glucose makes up the bulk of what sugar does occur and there are smaller amounts of cane sugar and fructose ; but during *cell enlargement* fructose and, to a less extent, cane sugar increase more rapidly in amount than glucose, until they make up the bulk of the total sugars present. Starch appears during *cell enlargement* and increases up to the middle of this period, then it decreases and finally disappears before *maturity*. The rate of disappearance of starch increases on picking and there are decreases in cane sugar and total glucose. During *maturity* total fructose suddenly begins to fall but cane sugar increases. During *senescence* all three sugars decrease in amount. The acidity becomes steadily less throughout the life of the apple (F. Kidd, Proc. Roy. Inst. 1934, **28**, 351 ; M. Onslow, F. Kidd, C. West, Rep. Food Investigation Board, 1931, 52 ; H. K. Archbold, Ann. Bot. 1932, **44**, 408). Total nitrogen increases steadily throughout the life of the apple, making up 0·02–0·05% of the fresh weight. The proportion of total nitrogen present as protein increases steadily from about 20% to as much as 80% at the end of storage life (A. C. Hulme, Rep. Food Investigation Board, 1932, 75 ; 1934, 135). Ripe apples give off minute traces of ethylene, which causes other unripe apples to ripen ; hence apples of different degrees of maturity, if stored together, tend to ripen all at the same time (R. Gane, Rep. Food Investigation Board, 1934, 122). Traces of acetaldehyde and ethyl alcohol are also evolved from ripe fruit (A. C. Hulme, Rep. Food Investigation Board, 1933, 70). Some of these volatile products are toxic and tend to cause damage ; this may be avoided by very thorough ventilation or by wrapping in tissue paper impregnated in odourless mineral oil (Kidd, *l.c.*). A variety of cultural conditions affect the storage life of an apple ; adequate dressings of potassic manures prolong, and excessive dressings of nitrogenous manures decrease, storage life (T. Wallace, Proc. First Imperial Horticultural Conference, 1930, 9). Apples should be picked before reaching maturity. The life of all varieties is prolonged by keeping the temperature a few degrees above freezing-point, and that of some varieties may be prolonged by a less drastic lowering of the temperature, combined with an increase in the carbon dioxide content of the atmosphere ; optimum temperature and composition of atmosphere have been worked out for all the main commercial varieties and the necessary storage conditions are maintained both in ships' holds and in stores kept by British and other growers (F. Kidd, C. West, Leaflet 6, Food Investigation Dept. Sci. and Ind. Res. 1935).

Following on the chemical work of M. H. Carré (Ann. Bot. 1925, **156**, 811) and others, M. H. Carré and A. S. Horne (Ann. Bot. 1927, **162**, 193) have studied in detail by microscopical and microchemical methods the changes in the pectic constituents during the life of the apple under various normal and abnormal storage conditions.

Apples contain the antiscorbutic vitamin C. Varieties vary considerably in their potency, some being twice as rich as others (M. F. Bracewell, F. Kidd, C. West, S. S. Zilva, Biochem. J. 1931, **25**, 138 ; M. B. Crane, S. S. Zilva, *ibid.* 1932, **26**, 2177). The potency is not appreciably less after 5 months' storage at 5° C. (M. F. Bracewell, F. Kidd, C. West, S. S. Zilva, *l.c.*), and they preserve their potency after being cooked (M. F. Bracewell, E. Hoyle, S. S. Zilva, Biochem. J. 1930, **24**, 81). The concentration of the vitamin decreases from the skin inwards, there being 6 times as much in the skin as in the flesh near the core (M. F. Bracewell, F. Kidd, C. West, S. S. Zilva, *l.c.*).

Apple wood, because of its hardness and toughness, is used for turning and for a number of other purposes for which these two properties are necessary. W. A. R.

APPLE JACK. The alcoholic distillate from cider consumed as a liqueur. The term is also used for the liquid obtained by repeated partial freezing of cider. This contains the concentrated extractive substances as well as alcohol.

APPLE-PULP is a term applied in the jam and cider industries to three distinct materials.

In the jam industry it refers to the product obtained by subjecting apples—usually those of culinary varieties—to the action of steam until the fruits are thoroughly cooked and disintegrated to a viscous pulp of semi-liquid character. The degree of fluidity is determined partly by the amount of juice contained in the fruit and partly by the quantity of steam condensed in the mass during the cooking of the apples. The cooked mass is passed through a sieving machine which removes the fragments of peel, core, and pips. This treatment yields the article technically known as apple-pulp, which is uniform in texture and constitutes a mixture of apple-juice, condensed steam, cell walls of the tissues of the flesh of the fruit and dissolved pectinous substances extracted by the cooking from the cellular material. The value of the pulp to the jam industry resides in the pectin content, which is relatively high, although a very variable figure in different samples. It is used to aid the " setting " or " gelling " of jams, for which the interaction of pectin, sugar and acid is responsible.

In the cider industry apple-pulp is commonly termed "Pomace." Strictly, pomace is the disintegrated mass of apple tissue resulting from the milling or crushing of the fruit prior to the expression of the juice. More often, however, the name is applied to the residue remaining after the juice has been extracted as far as possible by the cider presses. This is sometimes described as "pressed" pomace to distinguish it from the former.

Pressed pomace is a by-product of cider-making and is utilised for a variety of purposes. Its chemical composition varies considerably according to the kinds of apples from which it is produced and the extent to which the juice has been removed in the press. The following data give a fair indication of the range of its percentage composition : water 68·4–78·1, fat (ether extract) 0·82–1·43, protein 1·03–1·82, crude fibre 4·42–10·5, ash 0·56–2·27, carbohydrates (sugar, etc.) 9·5–22·0.

In this form most cattle and other farm livestock eat it readily, and it is a satisfactory feeding stuff if given as an adjunct to more concentrated foods. It must be used fresh, for it undergoes decomposition—acetification particularly—so rapidly as to be unfit for consumption in two or three days in warm weather. It may be preserved for a considerable period if mixed with salt and tightly pressed in a silo.

It is more effectively preserved by desiccation. This is now done commercially on a large scale in specially constructed drying machines. It will keep indefinitely if the moisture content is reduced to 10%. The dried material is utilised extensively for the production of pectin extracts required in jam-making. It also serves as a useful ingredient in the manufacture of compound cattle cakes and poultry food in which it acts as a diluent for the more concentrated components.

Pressed pomace also makes an excellent manure if mixed with half its weight of lime to neutralise acids. The ash usually contains 0·2–0·6% potash, 0·4 to 0·7% phosphoric acid, and 1·6–1·7% nitrogen (Barker and Gimingham, J. Board Agric. 1915, **22**, 851, and Barker, J. Min. Agric. 1933–34, **40**, 710). *See* CIDER. B. T. P. B.

APRICOT. Fruit of *Prunus armeniaca.* The average percentage composition of the edible flesh of fresh apricots is given as :

Water.	Protein.	Malic acid.	Tannin.
86·3	1·02	1·27	0·07
Total sugar.	**Sucrose**	**Fibre.**	**Ash.**
7·01	3·53	0·80	0·67

Small amounts of citric acid are also present and contribute to the flavour of the fruit. The latter is said to be imitated by a mixture of *iso*-amyl butyrate and *iso*-amyl alcohol. The ripening process on the tree is marked by a very rapid increase in reducing sugars. Appreciable amounts of sucrose occur only in the full-ripe fruit.

The ash of Californian apricots consists of: K_2O 59·36%, Na_2O 10·26%, CaO 3·17%, MgO 3·68%, MnO_2 0·37%, P_2O_5 13·09%, SO_3 3·63%, SiO_2 5·23%, Cl 0·45%, Fe_2O_3 1·68%.

From 6–11% of the whole fruit is represented by the stone and of this 22–25% consists of the kernel. The latter contains amygdalin and yields, by pressure, 35% of oil which, after filtration and decolorisation with fuller's earth or charcoal, shows the following characteristics: d^{15} 0·915–0·920, solidification point −14° to −20°, saponification value 192, iodine value 104, fatty acids 1·6% (Tilgner, Konserven. Ind. 1931, **18**, 257). The oil is sometimes found as an adulterant of almond oil, from which it may be distinguished by giving a red colour when dissolved in chloroform and treated with fuming nitric acid. Under these conditions almond oil yields a yellowish-brown colour.

The vitamin-A content of apricots is notably high in comparison with other fruits. Brockmann (Z. physiol. Chem. 1933, **216**, 45) records the presence of considerable amounts of β- and some γ-carotene.

Apricots are preserved by splitting and drying either in the sun or artificially. The latter process is usually preferred as yielding a more standardised product and minimising the destruction of vitamins. "Sulphuring," *i.e.* treatment with sulphur dioxide, serves to avoid darkening in colour during the drying process and improves the storage qualities of the product.

The average percentage composition of dried apricots is:

Water.	Protein.	Malic acid.	Invert sugar.
30	4·5	4·8	20

Sucrose.	Fibre.	Ash.
17·8	23	3·6

The dried fruit contains 0·03% of boric acid (Dodd, Analyst, 1929, **54**, 15). A. G. Po.

APYRON. *Lithiopyrin*, also *Hydropyrin. Tyllithin.* Trade name for lithium acetylsalicylate, $AcO{\cdot}C_6H_4{\cdot}COOLi$. Antirheumatic.

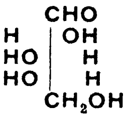
AQUA REGIA. *Nitromuriatic acid*; *Königswasser.* A name given by the alchemists to a mixture of nitric and hydrochloric acids, originally prepared by dissolving sal ammoniac in strong nitric acid, and used by them as a solvent for gold, sulphur, etc. Usually made by mixing 1 vol. of concentrated nitric acid with 4 vols. of concentrated hydrochloric acid. The mixture is at first colourless, but gradually—especially on heating—acquires a deep orange-yellow colour, due to the formation of nitrosyl chloride and free chlorine:

$$HNO_3+3HCl=NOCl+Cl_2+2H_2O$$

The solvent action of aqua regia appears to be mainly due to the free chlorine.

AQUARESIN G.M. Ethylene glycol boriborate.

ARABINOSE, $C_5H_{10}O_5$.

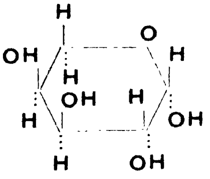


The pentose, l-arabinose, is widely distributed in plants, though it is not known in the free condition. It is a constituent of some glycosides—the vicianosides—and of pectin and particularly of the polymeric arabans or plant gums.

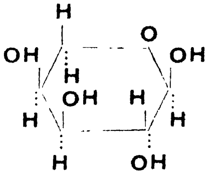
Preparation.—A solution of gum arabic, or allied gum (dextro-rotatory, and yielding little mucic acid by the action of nitric acid, by preference), containing 30–40 g. of the gum and 2–3 c.c. sulphuric acid in 100 c.c., is boiled for 7–12 minutes, cooled, the acid neutralised with calcium or barium hydroxide or carbonate, and alcohol, sp.gr. 0·83, added as long as a precipitate is produced. This precipitate soon settles, leaving the alcoholic solution clear. On distilling off the alcohol and evaporating to a syrup, arabinose crystallises out. The substance is obtained in well-defined rhombic prisms, with monoclinic termination, by recrystallising from water. With some gums the digestion of the acid solution can be continued for 2 hours with increased yield of arabinose, and without impairing the purity of the product. The crystals are anhydrous, m.p. 160°.

Another preparative source of the sugar is sugar-beet pulp (Harding, Sugar, 1922, **24**, 656). The pulp is boiled with 1½% sulphuric acid for 1½ hours, neutralised with barium hydroxide, and purified in the usual manner with basic lead acetate. The solution is concentrated and double its volume of alcohol added. The sugar is crystallised from glacial acetic acid or from alcohol containing 1% of nitric acid; yield 4–5%.

It exhibits muta-rotation, α-arabinose having the initial rotatory power $[\alpha]_D$ +175°, decreasing to +104°. β-Arabinose has not been isolated. The α- (trans) form preponderates in the equilibrium mixture, being present to the extent of 58%.



α-Arabinose.



β-Arabinose.

Arabinose is not fermented by yeasts, but organisms which ferment it are widely distributed, *e.g.* acetic and lactic fermentations of silage.

Bromine oxidises it to l-arabonic acid, $C_5H_{10}O_6$, which crystallises as the lactone $C_5H_8O_5$, m.p. 95°–98°, $[\alpha]_D$ −73·9°. Nitric acid forms oxalic acid as the final product, but in dilute solution firstly arabonic acid and secondly l-trihydroxyglutaric acid, m.p. 127°, are formed. On reduction, amongst other products, l-arabitol, m.p. 102°, is formed, which is optically inactive, but becomes lævo-rotatory in presence of borax.

Arabinose shows the usual aldose reactions; characteristic for its identification is an almost insoluble diphenylhydrazone, m.p. 218° (Tollens, Ber. 1904, **37**, 312 ; 1906, **39**, 3576).

The other hydrazones have the following melting-points: phenyl 151°, *p*-bromophenyl 150°, *a*-methylphenyl 161°, *a*-ethylphenyl 153°, *a*-amylphenyl 120°, *a*-allylphenyl 145°, *a*-benzoylphenyl 170°, *β*-naphthyl 141°. Arabinose phenylosazone, m.p. 160°, is prepared similarly to the glucose compound. It is slightly more soluble, and when boiled with benzaldehyde arabinosone is formed. The *p*-bromophenylosazone has m.p. 196°–200°.

d-Arabinose, sometimes called *aloinose*, has been prepared only twice from natural sources, viz. from the glycoside barbaloin (Léger, Compt. rend. 1910, **150**, 695). It is also a constituent of the polysaccharide of tubercle bacilli (Anderson, Z. physiol. Chem. 1930, **191**, 172). It can be obtained synthetically from *d*-glucose by the various degradation methods. It is unusual for both stereoisomeric forms of a sugar to be found in nature. E. F. A.

ARABITOL, $C_5H_{12}O_5$, the alcohol corresponding to Arabinose. *d*-Arabitol has been found in a fungus *Ustilago virens* which infects rice in Japan (Yabuta and Sumiki, J. Agric. Chem. Soc. Japan, 1933, **9**, 492) and in the lichen *Lobario pulmonario* (Nolan and Keane, Nature, 1933, **132**, 281). E. F. A.

l-**ARABONIC ACID** *v.* ARABINOSE.

ARACHIDIC ACID, eicosoic acid,

$$CH_3[CH_2]_{18}COOH,$$

occurs in butter, in human fat (0·3%), in higher fractions of mineral oil distillates, in peanut oil, linseed oil, soya bean oil, earth-nut oil (from *Arachis hypogœa*, Linn.), and in the fruit of *Nephelium lappaceum* (Grössmann, Annalen, 1854, **89**, 1 ; Oudemans, Z. f. Chem. 1867, 256 ; Wagner, Biochem. Z. 1926, **174**, 412). It may be synthesised from acetoacetic ester and octodecyl iodide (Schweizer, Arch. Pharm. 1884 [iii], **27**, 753), and may be prepared by treating behenolic acid with fuming nitric acid (Grössmann, Ber. 1893, **26**, 644) ; it has been shown to be identical with *iso*behenic acid formed by the degradation of lignoceric acid (Ehrenstein and Stuewer, J. pr. Chem. 1923 [ii], **105**, 199).

The acid has m.p. 77° (Calo, Atti iv congr. naz. chim. pura appl. 1933, 681) and is sparingly soluble in alcohol (solubility in 90% alcohol, 0·022% at 15° and 0·045% at 20°). For heat of crystallisation, *see* Garner, Madden, and Rushbrooke (J.C.S. 1926, 2491). The lithium and sodium salts have been obtained by boiling the acid with lithium or sodium carbonate, and the potassium salt by dissolving the acid in hot alcoholic potassium hydroxide with subsequent cooling and dilution.

Methods of detection and isolation of arachidic acid depend on the sparing solubility of the potassium salt in acetone (Fachina and Dorta, Chem.-Ztg. 1914, **38**, 18 ; Pritzker and Jungkunz, Z. Unters. Nahr. Genussm. 1921, **42**, 232) or on the insolubility of the lead salt in alcohol (Kreis and Roth, *ibid.* 1913, **25**, 81). The *phenacyl ester*, m.p. 85°–86°, p-*chloro*- and p-*bromophenacyl esters*, m.p. 86° and 89° respectively, also provide convenient means of identification (Hann, Reid, and Jamieson, J. Amer. Chem. Soc. 1930, **52**, 818).

The *anhydride* has m.p. 77·5°–77·7°, the *methyl ester* m.p. 54·5°, and the *ethyl ester* m.p. 50°, b.p. 284°–286°/100 mm. ; for the *butyl ester, see* U.S.P. 1613366. G. F. B.

ARACHIN is a globulin which occurs in ground-nut (*Arachis hypogœa*) meal to the extent of 25%, being accompanied by 8% of another globulin, *conarachin* (Johns and Jones, J. Biol. Chem. 1916, **28**, 77 ; 1918, **36**, 491 ; Jones and Horn, J. Agric. Res. 1930, **40**, 673). Its nutritive value is very low (Sure, J. Biol. Chem. 1920, **43**, 443 ; Jones and Waterman, *ibid.* 1922, **52**, 357). Arachin has $[a]_D^{20}$ −39·5°, conarachin $[a]_D^{20}$ −42·7° (Jones and Horn, *l.c.*).

ARACHIS OIL (*ground-nut oil*) is obtained from the seeds of *Arachis hypogœa*, Linn. (*N.O.* Leguminosæ), the fruits of which are known in commerce as "earth-nuts," "peanuts," or "monkey-nuts."[1] The cultivation of the arachis plant is so ancient that its origin is uncertain, but it is generally believed that the home of the plant was in Brazil, whence it was introduced into Africa and Asia during the sixteenth century. The chief producing countries which export ground-nuts for the production of oil are India, West Africa, and China; besides the large quantities of nuts grown in these countries for domestic use as food, or for oil-manufacture, considerable crops of groundnuts are produced for local consumption in other parts of Africa—Mozambique, Tanganyika, Anglo-Egyptian Sudan, etc.—the Argentine, the E. and W. Indies, Spain, Japan, and Malaya, etc. The United States is exceptional, in that practically the whole of the domestic crop, which amounts to about 600,000 tons (decorticated basis)[2] is consumed as nuts, about 400,000 tons being harvested and used for human food in confectionery, and pea-nut butter, while the balance of the crop is left in the ground to be "hogged off" as food by pigs. Accurate production figures for every country are not available, but the annual world production of arachis nuts may be estimated at about 6,000,000 tons of nuts in shell ; India, with a production of about 3,000,000 tons per annum accounts for about half the world output and more than double the estimated output of China, her largest competitor.[1] Export balances from the principal exporting areas, which rose from an annual average of 600,000 tons (decorticated basis) in the pre-War quinquennium to about 1,500,000 tons per annum between 1928 and 1931, fell to about 1,200,000 tons in 1932–1933 : the British Empire (chiefly India) supplies about 60–70% of the total exports entering world trade, for which France, Germany, and England are the chief markets. Arachis oil is chiefly expressed in the South of Europe (Marseilles and Trieste) : France, in which the modern arachis oil industry was first developed, is still the largest importer of the nuts, absorbing some 60% of the total exports (*cf.* 70% from 1909–1913). Smaller quantities of ground-nuts are processed in Holland and Germany and meet the long-established Continental demand for edible arachis oil for margarine, and for table and culinary use ; the lower grades of oil constitute an important and characteristic ingredient of Marseilles soap and other soaps of Southern Europe. In the United Kingdom, however, where the interest of the crushing industry used to be centred in the production of linseed and cottonseed cattle-cake, the expression of ground-nuts has only become of importance since the War, imports amounting to about 130,000 tons per annum in 1933. In commerce a distinction is made between "undecorticated" and "decorticated" (shelled) nuts : as a rule, the nuts are exported in the undecorticated state from producing areas, such as West Africa and Gambia, which are relatively near to their markets, whilst in the case of remoter areas, *e.g.* China, India, Mozambique, the nuts are usually decorticated (shelled) before shipping in order to save weight and space in transport. The finest qualities of edible oil are prepared from undecorticated nuts, only the lower grades of oil from the second and third pressings being used for technical purposes. A good quality of oil can be recovered from decorticated seeds, but as they undergo some fermentative deterioration during transport, they cannot be used for the preparation of the best edible oil, and are mostly worked up for soap oil.

---

[1] The term "nut" is a popular misnomer: strictly speaking, the *Arachis* fruit is a pod ("legume") containing 2 (rarely 3 or 4) seeds; the name "earth-nut" is a reference to the characteristic habit of the plant, the seed-pods of which bury themselves in the ground during ripening. On the classification of ground-nut varieties, *cf.* T. R. Hayes, Trop. Agric. 1933 (10), 318 ; A. Chevalier, François, and Rambert, Rev. Bot. appl. d'Agric. trop. 1929, **9**, nos. 90, 91.

[2] For purposes of comparison, 100 tons of undecorticated nuts may be taken as equivalent to 75 tons of kernels (decorticated nuts) or to 30 tons of oil *plus* 70 tons of undecorticated cake ; 100 tons of decorticated nuts yield 40 tons of oil and 60 tons of decorticated cake.

The following figures, due to Fleury ("L'arachide, principalement celle de la Sénégambie," Bordeaux, 1900, *cf.* François, Rev. Bot. appl. d'Agric. trop. 1934, No. 156, p. 621), illustrate the percentage composition of the kernel and shell (figures in brackets) of ground-nuts from various sources : oil 41–55 (1·3–3·8), moisture 3·9–15·8 (7·8–20·6), proteins 35·4–23·0 (5–8·2), nitrogen 4·25–5·50, fibre 1·6–4·9 (7·8–20·6), non-nitrogenous extractive matters (carbohydrates) 6–21·9 (10·6–39), ash 1·9–4·3 (3–4·6). The shell (pod) constitutes from about 25–30% of the whole fruit ("nut").

The undecorticated nuts are shelled by special machinery, the red skin surrounding the kernel being removed by an air-blast.[2] The separated, cleaned kernels are ground in the usual manner and subjected to hydraulic pressure : as the kernels are rich in oil, the expression is usually performed in two or three stages. In France a preliminary expression is often conducted at the ordinary temperature, yielding a "cold-drawn" oil of which the best qualities are used as a salad and cooking oil under the name "huile surfine de Rufisque, — de Gambia," etc. The first hot expression at about 30°–32°C. yields an oil which is refined for edible purposes in the sardine-packing and margarine industries. The slightly inferior oil produced by a second hot expression (at 50°–55°C.) is chiefly used for soap making. Arachis oils are also used as a minor ingredient of lubricating oil and to a small extent in the woollen-textile industry. Promising results have been obtained in attempts to use locally-produced arachis oil as a fuel for semi-Diesel and Diesel engines (both stationary and automobile engines) in tropical districts, which are remote from supplies of petroleum fuels (*cf.* Gauthier, Bull. Mat. Grasses, 1931, **15**, 232 ; Rev. Combus. liq. 1933, **11** (No. 101), 19 ; 1935 (13), 129). The expressed arachis cakes from decorticated nuts serve as an excellent cattle food, for they contain the highest amount of proteins of all known oil cakes ; moreover, these proteins are most easily digested. Cakes from undecorticated seed are similarly employed. Occasionally solvent extraction is employed for the recovery of oil from low grade or damaged seed, or when the highest possible yield of oil is required : the residual meal, which is almost oil-free, may be used as fertiliser.

The following analyses by Jamieson, Baughman, and Brauns (J. Amer. Chem. Soc. 1921, **43**, 1372—American oils of two types), and by Hilditch and Vidyarthi (J.S.C.I. 1927, **46**, 172T —African oils) illustrate the composition of the fatty acids of arachis oil :

Fatty acids %	American.		W. Africa.	Senegal.
Palmitic .	8·2	6·3	6	7·3
Stearic .	6·2	5	3	2·6
Arachidic .	4	3·3	3·5	2·6
Lignoceric	3·1	2·6	3	2·6
Oleic . .	53	60·6	71·5	65·7
Linolic .	25	21·6	13	19·2

Although the saturated acid content remains fairly steady (14–20%), the linolic–oleic acid ratio appears to vary considerably in different samples. Thiocyanometric analysis (Kaufmann, Z. angew. Chem. 1928, **41**, 1046) indicated variations from 58–80% of oleic and 10–25% of linoleic acid (*cf.* Heiduschka and Felser, Z. Unters. Nahr. Genussm. 1922, **43**, 381). Neither Jamieson nor Hilditch was able to detect "hypogæic acid" nor any isomer of oleic acid. There is still some uncertainty as to the composition of the higher saturated acids of arachis oil, as the separation of these acids is exceedingly difficult: their melting-points lie close together, and both the acids and their derivatives form mixtures which simulate the behaviour of simple individuals having carbon chains of intermediate length. Ehrenstein and Stuewer (J. pr. Chem. 1923 [ii], **105**, 199 ; *cf.* Meyer, Brod, and Soyka, Monatsh. 1913, **34**, 1118), followed by Levene and Taylor (J. Biol. Chem. 1924, **61**, 157), regarded *lignoceric acid* as a branched-chain C_{24} acid, and the *arachidic acid* of arachis oil as a branched-chain C_{22} acid. In view of later work, including that of Taylor himself (J. Biol. Chem. 1931, **91**, 541 ; *cf.* Heiduschka and Pyriki, Pharm. Zentr. 1925, **66**, 1 ; Cohen, Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 630), and the X-ray evidence, it is more probable that only *straight-chain* acids are concerned in the mixture. Thus Jantzen and Tiedcke (J. pr. Chem. 1930 [ii], **127**, 277), using a refined method for the fractional distillation of the methyl esters, isolated n-*eicosoic* (C_{20}, arachidic [1]), n-*docosoic* (C_{22}, behenic), and n-*tetracosoic* (C_{24}, lignoceric, m.p. 84°–85°C.) acids (*cf.* Taylor, *l.c.*).

---

[1] The statistical information given in this article is drawn from the exhaustive statistical review, "Ground-nut Products (Production and Trade)," Vol. III of the "Survey of Oilseeds and Vegetable Oils," prepared by the Intelligence Branch of the Imperial Economic Committee (IEC/S/2 : H.M.S.O., Oct., 1934).

[2] If not wasted, the shells are used as manure, as fuel in oil mills and cotton ginneries, for polishing in the tin-plate industry, or as bait in the French sardine-fishing industry, or they may be ground with molasses for cattle-food ("Ground-nut Products," *l.c.*).

Cerotic acid (C_{26}) also appears to be present in small amounts (*cf.* Holde and Godbole, Ber. 1926, **59**, 36 ; Holde, Bleyberg, and Rabinovitch, Chem. Umschau, 1929, **36**, 245 ; Holde and Bleyberg, Z. angew. Chem. 1930, **43**, 897 ; Morgan and Holmes, Nature, 1926, **117**, 624 ; Francis, Piper, and Malkin, Proc. Roy. Soc. 1930, A, **128**, 214).

X-ray examination of the acids of arachis oil : the lines in the X-ray diagram which suggest the presence of fatty acids having an odd number of carbon atoms in the molecule are most probably produced by difficultly-separable mixtures of the even-numbered acids of high molecular weight.

The considerable content of arachidic and lignoceric acids distinguishes arachis oil from all the other commercial oils which otherwise resemble it,[2] and as these acids can be determined quantitatively, the separation and determination of "crude arachidic acid" (as originally proposed by Renard (Compt. rend. 1871, **73**, 1330)) furnishes an excellent means of identifying arachis oil and determining its proportion in admixture with other oils, such as olive oil, which may have been adulterated with it (*cf.* Evers, Analyst, 1912, **37**, 487 ; also Brit. Pharmacopœia, 1932, p. 576 ; Thomas and Yu, J. Amer. Chem. Soc. 1923, **45**, 113) : for shortened versions of the quantitative test which are used for the qualitative detection of arachis oil, *cf.* Bellier, Ann. chim. anal. 1899, **4**, 4 ; Evers, Analyst, *l.c.* ; *ibid.* 1937, **62**, Feb.–March. ; Shelley, Analyst, 1925, **50**, 182, 498 ; Richmond and others, *ibid.* 285 ; Powell, *ibid.* 395.

Cold-drawn and refined arachis oils are nearly colourless ; the lower qualities are pale yellow in colour but become decolorised on exposure to sunlight. The cold-drawn oil has a pleasant nutty flavour recalling that of kidney-beans. The specific gravity of commercial arachis oil is usually about 0·917–0·919 at 15°C., but Sadtler (Amer. J. Pharm. 1897, **69**, 490) reported a value as low as 0·911 for oil from African nuts, whilst specific gravities of 0·9223–0·9256 and 0·919–0·922 have been recorded for oils from Indian (Crossley and Le Sueur, J.S.C.I. 1898, **17**, 989) and American (Jamieson and Baughman, Cotton Oil Press, May, 1922) ground-nuts respectively. The iodine value usually lies between 87 and 100, but extremes of 83·3 (Rufisque nuts, Tortelli and Ruggieri) and 105 (Oliveri) are on record ; Margaillan and Favier (Chim. et Ind. 1934, **31**, Spec. No., p. 898) have reported iodine values of 101 and 103 for oils from Argentinian seeds.

As the iodine value of arachis oil lies so near to that of olive oil, adulteration, or even substitution, of the latter by arachis oil takes place on an extensive scale (for references to the detection of arachis oil, *see* above). Arachis oil itself is liable to be adulterated with sesame oil, added partly with the object of preventing the solidification of the oil when exposed to moderately low temperatures ; the addition of sesame oil may be detected by the Baudouin colour test (*see* SESAME OIL).

On standing a few degrees above the freezing-point, arachis oil deposits a "stearine" which does not readily settle out as a crystalline mass, and therefore cannot be removed in the usual manner by filtration or expression. Hence, in order to "demargarinate" ("winterise") arachis oil, it is necessary to allow it to stand in the cold for a prolonged time before the clear supernatant oil can be drawn off from the deposited "margarine d'arachide" which has settled out. E. L.

ARAGONITE. The orthorhombic form of calcium carbonate ($CaCO_3$), differing from the more common dimorphous form calcite (*q.v.*) in its greater density (sp.gr. 2·93), greater hardness (H. 3½), and in the absence of cleavage. It crystallises, together with calcite, from aqueous solutions of calcium carbonate containing carbon dioxide at temperatures above 18°, and the presence of various salts in the solution favours its growth. In nature it is deposited by thermal springs, for instance, those of Carlsbad in Bohemia, in the form of pea-like concretions, this variety of the mineral being known as *pisolite*. Another variety, called *flos-ferri* (flower of iron), is found as snow-white coralloidal forms in the iron mines of Styria. Crystals were first found embedded in red clay and gypsum in Aragon, Spain ; and divergent groups of spearlike crystals have been found in an iron (hæmatite) mine in west Cumberland. Fine groups of twinned prismatic crystals are met with in the sulphur mines near Girgenti in Sicily, and in the copper mines at Herrengrund in Hungary. A variety containing about 5% of lead carbonate is called *tarnowitzite* from its occurrence at Tarnowitz in Silesia. The calcium carbonate of pearls and mother-of-pearl is the aragonite modification.

---

[1] It may be noted in passing that the identity of the "arachidic acid" which constitutes 23% of the acids of Rambutan tallow with n-*eicosoic* acid is generally accepted (*cf.* Fat from the seeds of *Nephelium lappaceum* (*N.O.* Sapindaceæ), Morgan and Holmes, J.S.C.I. 1925, **44**, 219T ; Georgi, Malay Agric. J. 1929, **17**, 364).

[2] Apart from arachis oil the presence of notable amounts of arachidic and/or lignoceric acids has only been reported in Rambutan fat (*cf.* footnote [1] above) and in the fats from coral tree seeds (*Adenanthera pavonina* L. ; *cf.* Pieraerts, Mat. Grasses, 1930, 8785 *et seq.* ; Mudbidri, Ayyar, and Watson, J. Indian Inst. Sci. 1928, 11A, 173) the soap-nut tree seeds (*Sapindus trifoliatus* L. ; Paranjpe, J. Indian Inst. Sci. 1929, 12A, 179), pongam seeds (*Pongamia glabra*, Vent. : Desai, Sudborough, and Watson, J. Indian Inst. Sci. 1923, **6**, 93), Dhupa kernels (*Vateria indica* L. ; Hilditch, J.S.C.I. 1931, **50**, 468T), and kusum kernels (*Schleichera trijuga* Willd. : Dhingra and Hilditch, J.S.C.I. 1929, **48**, 281T), none of which is of commercial importance at present, nor resembles arachis oil in general physical properties.

When heated aragonite changes over into calcite, the transition point being 405°. A colour test for distinguishing aragonite and calcite is given by a solution of manganese and silver sulphates, which quickly deposits MnO_2+ Ag on aragonite (H. Leitmeier and F. Feigl, Tsch. Min. Mitt. 1934, **45**, 447). L. J. S.

ARALIA. Species (Fam. Araliaceæ). I. K. Gorter (Annalen, 1908, **358**, 327; A. 1908, i, 186) extracted chlorogenic acid, $C_{32}H_{38}O_{19}$, m.p. 206°–207° from East Indian species; this is not contained in European varieties (A. 1920, i, 358).

K. Mijaki (J. Biol. Chem. 1915, **21**, 507, 661) found choline, guanine, and xanthine in the shoots of A. cordata, used as food in Japan. A. W. van der Haar (Ber. 1922, **55** [B], 3041) isolated the sapogenin *araligenin*,

$$HO{\cdot}C_{25}H_{40}{\cdot}CO_2H,$$

m.p. 275°, from the leaves of *A. montana*. The saponins of *A. japonica* have been studied by A. Winterstein and G. Stein (Z. physiol. Chem. 1932, **211**, 5), those of *A. chinensis* by M. Kotake and Y. Kimoto, A. 1932, 516; *cf. also* 1140.

ARALIGENIN *v.* ARALIA.

ARAMAYOITE, $Ag_2S{\cdot}(Sb,Bi)_2S_3$ or $Ag(Sb,Bi)S_2$, occurs as black pseudo-tetragonal plates with perfect basal cleavage and steep pyramidal cleavages. X-ray examination proves it to be triclinic. Sp.gr. 5·602. The crystals show a brilliant metallic lustre, but this tarnishes on exposure to light and a white coating is formed on the surface. The mineral was found in the silver-tin mine at Chocayo in Bolivia (L. J. Spencer, Min. Mag. 1926, **21**, 156; K. Yardley, *ibid.* 163; E. Kittl, Rev. Minera Bolivia, 1927, **2**, 53). L. J. S.

ARANDISITE. Hydrous basic tin silicate, $3SnSiO_4,2SnO_2,4H_2O$, forms apple-green masses with fibrous massive structure and resinous lustre, sp.gr. 4·12. It occurs with cassiterite and quartz in a hydrothermal deposit in crystalline limestone near a contact with granite at Arandis, South-West Africa. It is decomposed by hot conc. H_2SO_4, but, unlike cassiterite, it is not reduced in the presence of zinc and acid (F. C. Partridge, Trans. Geol. Soc. South Africa, 1930, **32** (for 1929), 171). The extremely rare *stokesite*

$$[CaO{\cdot}SnO_2{\cdot}3SiO_2{\cdot}2H_2O]$$

is the only other known tin silicate mineral. L. J. S.

ARAROBA. *Goa Powder.* Crude chrysarobin (*q.v.*), a brown powder found in the trunk of a Brazilian tree *Andira araroba* (Fam. Leguminosæ). Used in the treatment of skin diseases.

ARBOTRINE, $C_{38}H_{55}O_6N$, m.p. 187°, is a physiologically active alkaloid from the bark of the stem and root of *Artabotrys suaveolens* Blume (Marañon, Philippine J. Sci. 1929, **38**, 259). G. B.

ARBUTIN, $C_{12}H_{16}O_7$, m.p. 200°. $[\alpha]_D$ $-63{\cdot}5°$. A colourless bitter glycoside obtained from the leaves of the bearberry (*Arbutus urva ursi*), many *Ericaceæ*, and varieties of the pear. It is often accompanied by methy-arbutin. It is hydrolysed by emulsin to glucose and hydroquinone. It is a powerful antiseptic and hence has a pharmacological value. The commercial arbutin can contain from 5 to 40% of the methyl ether; it may be purified by solution in alcohol, precipitation with potassium hydroxide, and decomposition with calcium carbonate. A better method is said to be to make use of the additive compound of arbutin and hexamethylenetetramine.

It has been synthesised by Mannich (Arch. Pharm. 1912, **250**, 547) from octobromoglucose and hydroquinone. E. F. A.

ARCAINE. *Tetramethylenediguanidine,*

$$NH:C(NH_2){\cdot}NH{\cdot}[CH_2]_4{\cdot}NH{\cdot}C(NH_2):NH$$

This base is found in the arginine fraction of *Arca Noæ* and was identified by Kutscher, Ackermann, Flössner, and Hoppe-Seyler (Z. physiol. Chem. 1931, **199**, 273, 277). It forms a *sulphate* (AB), m.p. 291° (decomp.); *picrate* (A_2B), m.p. 251°–254° (decomp.); *picrolonate* (A_2B), m.p. 303° (decomp.); *chloroaurate* ($B{\cdot}2\ HAuCl_4$), m.p. 170·5°; *chloroplatinate* ($B{\cdot}H_2PtCl_4$), m.p. 222°; *rufianate* (*quinizarin sulphonate*) ($B{\cdot}2\ C_{14}H_8O_7S$), m.p. 306°–311° (decomp.). The base gives a Sakaguchi reaction (*see* ARGININE). Like its homologues it lowers the blood sugar of warm-blooded animals. It is hydrolysed to putrescine and urea by saprophytic bacteria (Linneweh, *ibid.* 1931, **200**, 115). Zervas and Bergmann (*ibid.* 1931, **201**, 208) suggest that the natural origin of the base is diguanidovaleric acid. W. V. T.

ARCANITE *v.* APHTHITALITE.

ARCHIBROMIN. Trade name for monobromo-*iso*valerylglycolylurea.

ARCHIL or ORCHIL *v.* LICHENS.

ARCHIL SUBSTITUTES *v.* DYESTUFFS, AZO.

ARCHIODIN. Trade name for monoiodo*iso*valerylglycolylurea.

ARCTIC SPERM OIL *v.* BOTTLE-NOSE OIL.

ARDENNITE. A mineral consisting of vanadio-silicate of aluminium and manganese,

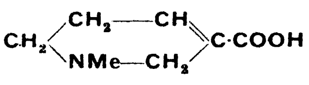
$$10SiO_2{\cdot}(V,As)_2O_5{\cdot}5(Al,Fe)_2O_3{\cdot}10(Mn,Mg)O{\cdot}6H_2O$$

containing 0·25–9·20% V_2O_5. The vanadium is partly replaced by arsenic (up to 10·30% As_2O_5), and in these varieties the colour is paler. It has been found only at Salm-Château, near Ottrez, in the Belgian Ardennes, where it occurs embedded in quartz veins in phyllites or slaty schists, and recently with manganese ores at Ceres in Piedmont. It forms yellow to brown aggregates of bladed or columnar crystals; these are orthorhombic with a perfect cleavage parallel to the brachypinacoid, and good cleavages parallel to the unit prism. Sp.gr. 3·58–3·66 ; hardness, 6–7. It is readily fusible with intumescence before the blowpipe to a black glass ; and is not attacked by hydrochloric and nitric acids, though slightly by sulphuric acid. L. J. S.

ARECA NUT, *Betel nut*, is the seed of the areca palm, *Areca Catechu*, Linn., a native of the Sunda Islands, cultivated in tropical India and the Philippines. It is often chewed in the Far East together with lime and the leaves of betel pepper, and is also used as a vermifuge. In America and Europe it is used in veterinary practice, against tape worm. Arecoline hydrobromide, m.p. 170°, is employed for this purpose, and is official in the German Pharmacopœia. The nuts contain six alkaloids, all more or less closely related : *Arecoline*, $C_8H_{13}O_2N$, the principal alkaloid, is a strongly alkaline liquid, b.p. 220°, and highly toxic (Meier, Biochem. Z. 1907, **2**, 415). Chemnitius (J. pr. Chem. 1927 [ii], **117**, 147) gives details for its extraction from betel nuts in 500 kg. quantities ; yield of pure hydrobromide 0·35–0·4%. Arecoline is the methyl ester of *Arecaidine* (*arecaine*),

$$C_7H_{11}O_2N,H_2O,$$

m.p. 232°, which is non-toxic and identical with *N*-methyl-Δ^3-tetrahydronicotinic acid,



synthesised by Wohl and Johnson (Ber. 1907, **40**, 4712). *Guvacine*, $C_6H_9O_2N$, m.p. 271°–272°, is a lower homologue in which the *N*-methyl is replaced by hydrogen ; hence the last two are both crystalline solids of neutral reaction. *Guvacoline* is guvacine methyl ester, b.p. 114°/13 mm., and an alkaline liquid which crystallises. For the constitution of these alkaloids, mostly discovered by Jahns (Ber. 1888, **21**, 3404), for the properties of their salts, and for earlier references, *see* Freudenberg (Ber. 1918, **51**, 1668), who thinks that perhaps only arecoline and guvacoline occur as such in the nuts. *Arecolidine*, $C_8H_{13}O_2N$, m.p. 110°, isomeric with arecoline, occurs in minute quantity in the mother liquors of technical arecoline hydrobromide, and is probably 3 : 4-dimethoxy-1-methyl-1 : 2-dihydropyridine (Emde, Apoth.-Ztg. 1915, **30**, 240). G. B.

ARECAIDINE, ARECAINE, ARECOLIDINE *v.* ARECOLINE.

ARECOLINE *v.* ARECA NUT.

ARGAL *v.* ARGOL.

ARGAN OIL is obtained from the kernels of *Argania sideroxylon*, Roem. et Schult., a tree growing in Morocco ; the meal obtained by roasting and grinding the kernels is kneaded with water in order to cause the oil to exude from the paste. The oil, which has an iodine value of 96–102 and (when fresh) resembles arachis oil in flavour and appearance, is extensively employed by the natives as an edible oil (in place of olive oil) and as a burning oil. The oil-cake contains a glucoside (saponin) "arganine" which, although it is toxic on intravenous injection, appears to be innocuous if administered orally to animals ; hence the fresh unfermented cake can be employed for fattening butchers' cattle (*cf.* M. Battino, Thesis, Paris, 1929 ; Bull. Mat. Grasses, 1929, **13**, 346 ; Girardet, Pharm. Acta Helv. 1927, **2**, 1 ; Moreau and Leulier, Bull. Sci. Pharmacol. 1918, **25**, 81). E. L.

ARGANINE *v.* ARGAN OIL.

ARGENTAMINE. Trade name for ethylenediamine silver nitrate or phosphate.

ARGENTINE. Finely divided spongy tin, made by reducing a weak solution of tin salt (120 g. in 60 litres of water) by zinc. The tin is collected in a sieve, washed with water, and dried at a gentle heat. Used for tin-plating and also for printing upon fabrics and paper (Pascher, Chem. Contr. 1883, [iii], **13**, 540).

ARGENTITE. A mineral consisting of silver sulphide, Ag_2S, and occurring as cubic crystals or as compact masses. It is blackish lead-grey in colour and perfectly sectile ; surfaces cut with a knife are bright and shining. Sp.gr. 7·3. Containing 87·1% of silver, it is a valuable ore of the metal when met with in quantity, as in the Comstock lode in Nevada and in Mexico.

Another form of silver sulphide is the orthorhombic *acanthite*, rarely found as distorted thorn-shaped (hence the name) crystals in silver mines in Bohemia, Saxony, and Colorado.

As shown by X-ray crystal analysis and by metallographic examination in reflected polarised light, silver sulphide is cubic above 180° and orthorhombic below this transition point. And it is seen that the well-formed cubic crystals of argentite consist of a complex lamellar aggregate of the orthorhombic form, *i.e.* they are paramorphs of acanthite after argentite (L. S. Ramsdell, Amer. Min. 1925, **10**, 286 ; R. C. Emmons, C. H. Stockwell, and R. H. B. Jones, *ibid.* 1926, **11**, 326 ; H. Schneiderhöhn, *ibid.* 1927, **12**, 326 ; J. Palacios and R. Salvia, Anal. Fís. Quím. 1931, **29**, 269, 514).

This fixes a point on the "geological thermometer," and when well-formed crystals of argentite or of acanthite are found, it is then known that they were deposited in the mineral veins at a temperature above or below 180°. L. J. S.

ARGENTOJAROSITE *v.* JAROSITE.

ARGHAN FIBRE. Pineapple fibre. A strong, soft fibre from *Ananas sativa* which has been used for twine and ropes. The plant cannot be grown advantageously to yield both fruit and fibre.

ARGINASE, a desamidase that decomposes arginine, guanidoaminovaleric acid, into ornithine and urea. It was first described by Kossel and Dakin (Z. physiol. Chem. 1904, **41**, 321). It is found in mammals' liver but not in birds' liver ; kidneys and testicles contain large amounts of it. It is present in certain plants.

Krebs (Z. physiol. Chem. 1932, **210**, 33) has shown that the production of urea in the liver from carbon dioxide and ammonia takes place in stages. In the first of these ornithine, αδ-diaminovaleric acid, is converted into citrulline,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2H,$$

which in the second stage takes up another molecule of ammonia to form arginine. In the final stage urea is split off by arginase and ornithine reproduced to take part in a new cycle. Hence the abundant amount of arginase in the liver and its absence from birds' livers, which do not synthesise urea. (For summary article, *see* Ergebnisse der Enzymforschung, 1934, **3**, 247.)

It has p_H 9·8, indicating that it acts on free as opposed to ionised base (Hunter and Dauphinee, Proc. Roy. Soc. 1924 [B], **97**, 209).

It hydrolyses γ-guanidinobutyric acid (Thomas, Z. physiol. Chem. 1913, **88**, 465). An arginase preparation of *Aspergillus niger* is said to split tetramethylguanidine into agmatine and urea (Kiesel, Z. physiol. Chem. 1922, **118**, 284). Arginine residues in the protein molecule are not attacked by it, though the guanidine group is free; yet half the guanidine groups of arginylarginine are hydrolysed, probably in the residue with the free carboxyl group (Edlbacker and Bonem, Z. physiol. Chem. 1925, **145**, 69); this is a somewhat surprising result.

The chemical nature of arginase has not yet been established. Preparations vary very much in their activity, as the enzyme is easily retarded or activated by other substances.

Arginase is activated:

(*a*) by metal complexes of SH-compounds such as the reduced glutathione with ferrous or cuprous ions (Waldschmidt-Leitz, Scharikova, and Schäffner, Z. physiol. Chem. 1933, **214**, 75). It is thought the active arginase is an oxidised form of the enzyme.

(*b*) by ascorbic acid in presence of small quantities of copper (Edlbacher and Leuthardt, Klin. Woch. 1933, **12**, 1843), when the activity can be increased 50%. Karrer and Zehender (Helv. Chim. Acta, 1934, **17**, 737) believe the activation by cystine, the ferrous ion, iodine, etc., to be due to the oxygen-binding capacity of the system.

The view predominates that the activation mechanism depends on a specific oxidation-reduction potential and is not a specific effect of the sulphydryl group. In other words, arginase can destroy arginine without a specific activator being necessarily present (Klein and Ziese, Z. physiol. Chem. 1932, **213**, 201; 1934, **229**, 209). E. F. A.

ARGININE, $C_6H_{14}O_2N_4$, *a-amino-δ-guanidino-*n*-valeric acid*,

$$NH:C(NH_2)\cdot NH\cdot[CH_2]_3\cdot CH(NH_2)CO_2H,$$

first isolated by Schulze and Steiger (Ber. 1886, **19**, 1177) from the etiolated germinated cotyledons of *Lupinus*, is the most widely distributed dissociation product of proteins, and can be obtained by hydrolysis of the proteins of seeds of *Lupinus luteus*, *Cucurbita pepo*, *Picea excelsa*, to the extent of 10%, *Abies pectinata*, *Pinus sylvestris*, and other conifers (Schulze, Ber. 1891, **24**, 276; Z. physiol. Chem. 1896, **22**, 411, 435; 1897, **24**, 276). According to Suzuki (Chem.-Ztg. 1899, **23**, 658) the arginine obtained from the seeds of conifers exists already formed, but in loose combination with protein, and is also produced synthetically in the plant from ammonium salts and nitrates, either in full or diffused daylight (Bull. Coll. Agric. Tokyo, 1900, **4**, 25). It is found in a number of plants, generally in company with asparigine, less often with glutamine, and also when neither is present (Stieger, Z. physiol. Chem. 1913, **86**, 268). It is found in soil (Schreiner and Shorey, J. Biol. Chem. 1910, **8**, 381; Schreiner and Lathrop, J. Amer. Chem. Soc. 1912, **34**, 1242), and in the blood under normal conditions (Abderhalden, Z. physiol. Chem. 1913, **88**, 478). For presence of arginine in hops, *see* Chapman (J.C.S. 1914, **105**, 1899). According to Skinner (Bied. Zentr. 1913, **42**, 213, from Proc. 8th Internat. Congress Applied Chem. 1912) it is produced in soil as a primary cleavage product of proteins and can take the place of nitrate in the soil. Arginine is also one of the constituents of the product of hydrolysis of proteins of animal origin; thus horn yields 2·25%, glue 2·60%, albumin from yoke of egg 2·3%, from white of egg 0·8%, from blood serum 0·7%; and casein 0·25% (Hedin, Z. physiol. Chem. 1894, **20**, 186), whilst the protamines *Salmine*, *Sturine*, *Clupeine*, *Scombrine*, *Cyclopterine*, and *Crenilabrine* yield arginine as the chief product of hydrolysis (Kossel, Z. physiol. Chem. 1896, **22**, 176; 1898, **25**, 165; 1899, **26**, 588; 1904, **40**, 565; 1910, **69**, 138). A convenient method of preparing arginine from gelatin with a yield of 60% is described by Bergmann and Zervas (*ibid.* 1927, **172**, 277). Cox precipitates arginine from a gelatin hydrolysate directly as flavianate (J. Biol. Chem. 1928, **78**, 475). Arginine can be separated electrolytically from other amino-acids (Foster and Schmidt, *ibid.* 1923, **56**, 545; J. Amer. Chem. Soc. 1926, **48**, 1709; Cox, King, and Berg, J. Biol. Chem. 1929, **81**, 755; Hendry and Johnson, Biochem. Z. 1930, **226**, 47). In cases of phosphorus poisoning arginine is found in the urine (Wohlgemuth, Z. physiol. Chem. 1905, **44**, 74), whilst the amount obtained from the liver is diminished (Wakeman, *ibid.* 335). The cleavage of arginine in plants and animals due to enzyme action is identical with that which occurs in putrefactive processes: ornithine and urea are produced (Kossell and Dakin, *ibid.* 1904, **41**, 321; 1904, **42**, 181; Ackermann, *ibid.* 1908, **56**, 305; Kiesel, *ibid.* 1912, **75**, 170, 196).

When arginine is heated with barium hydroxide it is decomposed into ammonia, urea, and *aδ-diaminovaleric acid* (ornithine, *q.v.*); cyanamide reacts with ornithine at the ordinary temperature to form arginine (Schulze and Winterstein, Z. physiol. Chem. 1898, **26**, 1; Ber. 1899, **32**, 3191), or with a-benzoylornithine to form the benzoyl derivative of arginine, and this is readily hydrolysed to arginine, which is thus proved to be *a-amino-δ-guanidino-*n*-valeric acid* (Sörenson, Ber. 1910, **43**, 643; *see also* Z. physiol. Chem. 1911–12, **76**, 94).

Arginine yields a copper compound,

$$Cu(C_6H_{14}O_2N_4)_2,$$

(Kober and Sugiura, J. Biol. Chem. 1912–13, **13**, 5).

Arginine crystallises in brilliant monoclinic plates (Haushofer, Z. physiol. Chem. 1887, **11**, 53) ; m.p. 238° (decomp.) (Vickery and Leavenworth, J. Biol. Chem. 1928, **76**, 701) ; it also crystallises with 1 H_2O in rhombohedra (Hedin, Z. physiol. Chem. 1895, **21**, 160) ; it dissolves readily in water, and is sparingly soluble in alcohol. Arginine contains an asymmetric carbon atom, and the dextrorotatory form is the natural product; the hydrochloride has $[\alpha]_D$ +12·5° in aqueous or +25·5° in hydrochloric acid solution. Arginine is strongly alkaline, and its solution absorbs carbon dioxide from the air ; it forms well-defined crystalline salts with acids, and compounds with certain metallic salts (Gulewitz, Z. physiol. Chem. 1887, **11**, 53). The *nitrate* $C_6H_{14}O_2N_4,HNO_3,\frac{1}{2}H_2O$ has m.p. 126° ; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$ has m.p. 151° ; the *hydrochloride* $C_6H_{14}O_2N_4,HCl,H_2O$ melts and decomposes at 209° when anhydrous ; the *dl*-aurichloride $C_6H_{14}O_2N_4,2HCl,AuCl_3,\frac{1}{2}H_2O$ has m.p. 105°–115° ; the *d*-arginine aurichloride $C_6H_{14}O_2N_4,2HAuCl_4,1\frac{1}{2}H_2O$ softens at 140° and melts at 160° (Weiss, Z. physiol. Chem. 1911, **72**, 490) ; of the *silver nitrate compounds* : $C_6H_{14}O_2N_4,AgNO_3,\frac{1}{2}H_2O$ decomposes at 164°, and $C_6H_{14}O_2N_4,AgNO_3,HNO_3$ melts and decomposes at 180° ; the *cupric nitrate compound* $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$ melts at 112°–114° or decomposes at 232°–234° when anhydrous ; the *copper sulphate compound* melts at 110° or decomposes when anhydrous at 235°–238° ; the *picrate* $C_6H_{14}O_2N_4,C_6H_3O_7N_3,2H_2O$, m.p. 205°, dissolves in 204·1 parts of water at 16° ; the *picrolonate* $C_6H_{14}O_2N_4,C_{10}H_8O_5N_4,H_2O$, m.p. 231°, dissolves in 1,124 parts of water, or 2,885 parts of alcohol at the ordinary temperature (Schulze and Steiger, Ber. 1886, **19**, 1177 ; Hedin, Z. physiol. Chem. 1894, **20**, 186 ; Gulewitz, *ibid.* 1899, **27**, 178 ; Steudel, *ibid.* 1903, **37**, 219 ; Reisser, *ibid.* 1906, **49**, 210) ; the *flavianate* (*2·4-dinitro-α-naphthol-7-sulphonate*), solubility 0·017, melts at 258°–260° (Kossel and Gross, *ibid.* 1924, **135**, 168). The aurichloride of a tetramethyl arginine, $C_{10}H_{24}O_2N_4Au_2Cl_8$, prepared by Engeland and Kutscher (Z. Biol. 1912, **59**, 415) crystallises in short needles which melt at 173°–175° to a clear fluid. Three methyl groups are in the side chain and one in the guanidine complex. For the products obtained by methylation of arginine with methyl sulphate under various conditions, *see* Zimmermann and Canzanelli (Z. physiol. Chem. 1933, **219**, 207) and Dirr and Lang (*ibid.* 1934, **225**, 79).

Certain acyl derivatives and esters of arginine have also been prepared : the *dibenzoyl derivative* $C_6H_{12}O_2N_4Bz_2$ crystallises in rhombic needles or prisms, m.p. 235° (decomp.) ; its *hydrochloride*, m.p. 218° ; d-*dibenzoylarginine ethyl ester hydrochloride*, m.p. 148°, has $[\alpha]_D^{20°}$ −8° (Gulewitz, *ibid.* 1899, **27**, 178 ; Felix and Dirr, *ibid.* 1928, **176**, 29). The *β-naphthalenesulphonyl derivative* $C_6H_{13}O_2N_4{\cdot}SO_2{\cdot}C_{10}H_7$ is a colourless powder, m.p. 88°–89° (Reisser, *l.c.*) ; *diarginylarginine* is isolated as the *dipicrate*,

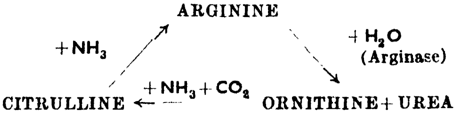
$$C_{18}H_{38}O_4N_{12}(C_6H_3O_7N_3)_2,2H_2O,$$

m.p. 207°, from the product obtained by hydrolysing pepsin extract with hydrogen fluoride ; *arginylarginine picrate*,

$$C_{12}H_{26}O_3N_8,C_6H_3O_7N_3,2H_2O,$$

m.p. 213°, is similarly obtained from gelatin (Hugouenq and Morel, Compt. rend. 1909, **148**, 236) ; *arginine methyl ester hydrochloride* has m.p. 195° (corr.) with decomposition ; the *picrate* forms lemon-yellow crystals, which melt and decompose at 218° (corr.) ; and the *nitrate* melts at 189° (corr.) (Fischer and Suzuki, Sitzungsber. K. Akad. Wiss. Berlin, 1904, **29**, 1333).

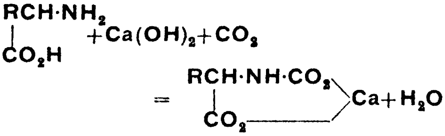
When arginine (hydrochloride or carbonate) is administered as a food, it suffers complete decomposition, and 37–77% of the nitrogen so given reappears as urea (Thompson, Z. physiol. Chem. 1905, **33**, 106), and the amount of arginine in the various organs shows no increase (Orglmeister, Beitr. Chem. Physiol. Path. 1905, **7**, 27). Administration of arginine increases the creatine content of muscle (Thompson, J. Physiol. 1917, **51**, 111, 347 ; Jansen, Arch. Néerland. physiol. 1917, **1**, 618). Ackroyd and Hopkins (Biochem. J. 1916, **10**, 551) suggest that arginine plays a special part in purine metabolism in the animal body. Ringer, Frankel, and Jonas (J. Biol. Chem. 1913, **14**, 539) suggest that succinic acid is an intermediate compound in the katabolism of arginine. More recently Krebs (Krebs and Henseleit, Z. physiol. Chem. 1932, **210**, 33 ; 1933, **217**, 191 ; **218**, 157) has put forward a scheme in which arginine is involved in the production of urea from ammonia in mammals. (Arginine has long been recognised as a source of urea ; Kossel and Dakin, *ibid.* 1904, **41**, 321 ; **42**, 181). The process can be represented as a continuous cycle thus :



The scheme is supported by the fact that arginase is abundant in the liver, which is the main if not the only organ of urea formation in the mammal (*see* ARGINASE).

Arginine gives the diacetyl reaction for proteins (Harden and Norris, J. Physiol. 1911, **42**, 333). An intense red colour is produced when a strongly alkaline solution of arginine is mixed with α-naphthol and treated with sodium hypochlorite. The reaction is ascribed to the free guanidine group (Sakaguchi, J. Biochem. Japan, 1925, **5**, 25, 133 ; *see also* Poller, Ber. 1926, **59** [B], 1927 ; Z. Biol. 1927, **86**, 309 ; Jorpes and Thoren, Biochem. J. 1932, **26**, 1504). Another reaction due to the guanidine group is the combination of arginine with benzoylacetyl in alkaline solution resulting in violet-coloured products (Lang, Z. physiol. Chem. 1932, **208**, 273).

Arginine is readily oxidised by hot calcium or barium permanganate yielding guanidine, γ-guanidinobutyric acid and succinic acid (Bénech and Kutscher, Z. physiol. Chem. 1901, **32**, 278, 413), and the estimation of the number of arginine groups in proteins is based on this reaction (Orglmeister, *l.c.*; Kutscher and Zickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, **28**, 624), the guanidine thus obtained being isolated in the form of its sparingly soluble picrate and either weighed as such or the nitrogen estimated in the usual way. Another method of isolating and estimating arginine is based on Siegfried's carbamino-reaction of amino-acids (Z. physiol. Chem. 1905, **44**, 85; **46**, 402; 1907, **50**, 171; Ber. 1906, **39**, 397), whereby the barium, strontium or calcium salt of the corresponding carbamic acid is formed when carbon dioxide is passed into a solution of the amino-acid containing excess of alkali earth hydroxide until the solution is neutral to phenolphthalein:



$$\begin{matrix}\mathrm{RCH{\cdot}NH_2}\\ |\\ \mathrm{CO_2H}\end{matrix} + \mathrm{Ca(OH)_2} + \mathrm{CO_2} = \begin{matrix}\mathrm{RCH{\cdot}NH{\cdot}CO_2}\\ |\\ \mathrm{CO_2}\end{matrix}\!\!>\!\mathrm{Ca} + \mathrm{H_2O}$$

The barium and strontium salts of these complex carbamic acids are much less readily soluble than the corresponding amino-acid, and afford a means of isolating the compounds (D.R.P. 188005, 1906). In order to estimate the amino-acid, the filtrate containing the calcium salt of the carbamic acid is decomposed by heating with boiled-out water into calcium carbonate and the amino-acid; the ratio CO_2 : N is determined by weighing the calcium carbonate thus precipitated, and estimating the nitrogen in the filtrate by Kjeldahl's method (Z. physiol. Chem. 1908, **54**, 423).

Van Slyke (J. Biol. Chem. 1911, **10**, 25) precipitates the arginine with phosphotungstic acid, decomposes the precipitate with barium chloride, and boils the filtrate gently with 50% potassium hydroxide for six hours; basing his estimation of arginine on the fact that it loses half of its nitrogen, in the form of ammonia, when boiled with dilute alkali.

Plimmer (Biochem. J. 1916, **10**, 115) decomposes the arginine with 20% alkali.

Wechsler (Z. physiol. Chem. 1911, **73**, 138) dissolves the dried phosphotungstate precipitate in a mixture of acetone and water, and then decomposes it with barium hydroxide. Details for the quantitative separation of arginine from protein hydrolysates are given by Kossel and Staudt (*ibid.* 1926, **156**, 270), who precipitate the base as flavianate, and by Vickery and Leavenworth (J. Biol. Chem. 1927, **75**, 115), who employ the picrate.

Arginine can be estimated in protein hydrolysates without isolation, either by decomposing it with arginase and estimating the urea formed (Jansen, Chem. Weekblad, 1917, **14**, 125; Hunter and Dauphinee, J. Biol. Chem. 1930, **85**, 627) or by application of Sakaguchi's reaction (Weber, *ibid.* 1930, **86**, 217; **88**, 353; Jorpes and Thoren, *l.c.*) or the benzoylacetyl reaction (Lang, *l.c.*).

dl-Arginine is readily produced by tryptic digestion of fibrin, or by heating *d*-arginine nitrate at 210°–220° for 15–20 minutes (Kutscher, Z. physiol. Chem. 1901, **32**, 476) or by heating *d*-arginine in 50% sulphuric acid in sealed tubes at 160°–180° for 33 hours (Reisser, Z. physiol. Chem. 1906, **49**, 210); it decomposes at 210° (Cathcart, Proc. Physiol. Soc. 1905, **32**, xv, xxxix); the *nitrate* $C_6H_{14}O_2N_4,HNO_3$ has m.p. 216°; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$, m.p. 151°; the *cupric nitrate derivative*,

$$2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O,$$

m.p. 228°–229°; the *silver nitrate derivative* $(C_6H_{14}O_2N_4,HNO_3)_2,AgNO_3$, m.p. 170°–172°; the *picrate* $C_6H_{14}O_2N_4,C_6H_3O_7N_3$, m.p. 200°–201°, is sparingly soluble (100 parts of water at 16° dissolve 0·22 part); the *picrolonate*,

$$C_6H_{14}O_2N_4,C_{10}H_8O_5N_4,$$

m.p. 248° (100 c.c. of water at 16° dissolve 0·03 g. of salt); the *β-naphthalenesulphonyl derivative*,

$$C_6H_{13}O_2N_4{\cdot}SO_2{\cdot}C_{10}H_7,\tfrac{1}{2}H_2O,$$

has m.p. 85°–90° (Reisser, *l.c.*). *Dibenzoylarginine* has m.p. 230° and the *ethyl ester hydrochloride* 143° (Felix and Dirr, Z. physiol. Chem. 1928, **176**, 207).

l-Arginine is formed by treating *dl*-arginine carbonate with the expressed juice of calf's liver; the *arginase* present in the extract destroys the *d*-arginine, and does not attack the lævo-isomeride. With the exception of the difference in optical activity, the salts of *l*-arginine are identical with those of the dextro-isomeride; *l-arginine hydrochloride* has $[\alpha]_D^{20°}$ $-20{\cdot}51°$ (Reisser, *l.c.*).

M. A. W. and W. V. T.

ARGOFERMENT. Trade name for a preparation of colloidal silver. Local antiseptic.

ARGOFLAVIN *v.* ACRIDINE DYESTUFFS.

ARGOL or **ARGAL** (*Tartre brut*, Fr.; *Weinstein*, Ger.). Crude potassium bitartrate, known as red argol (*Cremore di Vinaccia*), or white argol (*Cremore di St. Artimo*), according to whether it is deposited from the red or the white grape (*v.* TARTARIC ACID).

ARGON. Symbol A or Ar. Atomic weight and molecular weight 39·94. As long ago as 1785 Cavendish (Phil. Trans. 1785, **75**, 372) made experiments in order to determine whether the inert residue left after withdrawing oxygen, water, and carbon dioxide from air was homogeneous. He sparked a mixture of air and oxygen in presence of potash, for removal of the oxides of nitrogen produced, and absorbed the excess of oxygen with a solution of liver of sulphur. Only a small bubble of gas remained and this did not diminish in volume on further sparking with oxygen. Cavendish concluded "that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120 part of the whole."

Cavendish's work was overlooked for more than a century and attention was directed to it only after the discovery in 1893, by Lord Rayleigh (Proc. Roy. Soc. 1893, **53**, 134; 1894, **55**, 340), that the density of "atmospheric nitrogen" was ½% higher than that of nitrogen prepared by chemical means. This result gave a fresh indication of the existence of some hitherto undiscovered gas in the atmosphere. This gas was isolated by Ramsay and Rayleigh (*ibid.* 1895, **57**, 265) by sparking a mixture of air and oxygen over caustic potash and removing the excess of oxygen with pyrogallol. These authors obtained the same gas by passing air over heated copper and the residual gas over heated magnesium to remove nitrogen. The remaining gas, which had a density of approximately 20 and constituted nearly 1% by volume of the atmosphere, was called argon, owing to its remarkable chemical inertness. Ramsay and Rayleigh showed that the argon molecule was monatomic by measuring the ratio of the specific heats (Chem. News, 1895, **71**, 51).

Occurrence of Argon.—Argon occurs in the atmosphere to the extent of 1·3% by weight (Leduc, Compt. rend. 1896, **123**, 805) and 0·933% by volume. Measurements by Moissan (Compt. rend. 1903, **137**, 600) show that the concentration in air from widely separated localities is constant. Argon has also been detected in gas samples from many volcanic sources. Thus Allen and Zies (J. Franklin Inst. 1922, **193**, 29) found from 0·12–0·99% in gases from Alaskan volcanoes. Thorkelsson (Danske. Selsk. Skr. 1910, **8**, 182) found values as high as 2·15 volume % of argon in the gases from a volcanic source in Iceland. It has also been detected in volcanic rocks (Strutt, Proc. Roy. Soc. 1907, A, **79**, 436). Minerals which contain helium usually also contain argon. Among those which have been examined are cleveite (Runge and Paschen, Nature, 1896, **53**, 245), makalon (Ramsay and Travers, Proc. Roy. Soc. 1896, **60**, 442), granite, basalt and apatite (Sautier, Compt. rend. 1901, **132**, 58, 932). This argon is probably of atmospheric origin though its abundance, relative to helium, is very variable. Argon also occurs in natural gas, rain and river water, and in a large number of mineral waters (Bouchard, Compt. rend. 1895, **121**, 392 ; Troost and Ouvrard, *ibid.* 1895, **121**, 798 ; Moissan, *ibid.* 1902, **135**, 1278 ; Moureu, *ibid.* 1902, **135**, 1335 ; 1906, **142**, 1155 ; for collected data, *see* Gmelin's "Handbuch der anorganischen Chemie," 8th ed., 1926, Teil 1, "Edelgase").

Preparation.—(1) *By sparking air or impure argon with oxygen.*—This was the method employed by Cavendish (*v. supra*). It is laborious and is generally used only to remove the last trace of nitrogen from argon. The gas is confined over mercury and a small quantity of potash is introduced through a curved pipette. The sparks are passed between the ends of stout platinum wires. A suitable apparatus is described by v. Antropoff (Z. Elektrochem. 1919, **25**, 269). The sparking is usually continued for several hours after contraction has ceased ; the excess of oxygen is then absorbed either with pyrogallol or with phosphorus (Ramsay and Travers, Phil. Trans. 1901, A, **197**, 47). Strutt (Proc. Roy. Soc. 1907, A, **80**, 572) states that sparking will not remove the last trace of nitrogen. He used a glow discharge in potassium vapour for the final purification.

(2) *From "atmospheric nitrogen," the nitrogen being absorbed by a metal.*—Argon may be separated from nitrogen by circulating the gas over red-hot magnesium shavings, when magnesium nitride is produced. A tube containing 30 g. of magnesium will absorb 7–8 litres of nitrogen. It is important that the latter be free from oxygen, as otherwise nitrate will be formed and will block the tube. A more rapid absorption of the nitrogen is obtained by using a dry mixture of pure lime (5 parts) and magnesium dust (3 parts). When heated to redness this mixture forms metallic calcium, which reacts with nitrogen to form Ca_3N_2. Fischer (Ber. 1910, **43**, 1435) prepared argon by passing the impure gas containing nitrogen through a 2 cm. iron tube, 1·5 m. long, and containing red-hot calcium. The reactivity of calcium is variable ; absorption begins at 300°–400°. The optimum temperatures appear to be 400°–500° and near the melting-point of the metal (*cf.* Brandt, Z. angew. Chem. 1914, **27**, 424). Ruff and Förster (Z. anorg. Chem. 1923, **131**, 321) have described an apparatus for preparing pure argon from a technical 85% preparation by means of a calcium-calcium nitride alloy.

(3) *Removal of nitrogen by calcium carbide.*—The readiest method of preparing argon in quantity is to lead air slowly over a mixture of calcium carbide (90%) and calcium chloride (10%) heated in an iron tube to 800°–1000° (F. Fischer and O. Ringe, Ber. 1907, **40**, 1110 ; 1908, **41**, 2017). The absorbent is first heated in vacuum to drive off volatile material (tar, acetylene, etc.) which is always present. Both oxygen and nitrogen are absorbed from air by this mixture, forming carbon dioxide and calcium cyanamide respectively. The issuing gas is passed over red-hot copper oxide to burn any hydrogen, hydrocarbon, or carbon monoxide present, and the water vapour and carbon dioxide are then removed. Using 7 kilos of carbide, 11 litres of argon may be obtained in two days. The cyanamide process has been used in America for producing argon in quantity. The argon isolated by these methods is mixed with the other inert gases of the atmosphere.

Preparation of Argon by Liquefaction of Air.—The following table shows the composition of the air and the boiling-points of the constituents.

	He	Ne	N_2
Vol. % . . .	0·0005	0·0018	78·0
B.p. °C. . . .	−269	−246	−196

	A	O_2	Kr	X
Vol. % . .	0·932	21·0	0·0001	0·00001
B.p. °C. .	−187	−183	−152	−109

In the fractionation of liquid air argon is associated with oxygen and nitrogen, the three gases making up more than 99·99% of the total. Neon is isolated from the most volatile fraction, and krypton and xenon may be obtained in small amounts from the least volatile fraction.

Argon is prepared by fractionation in a rectification column of the normal type containing a number of plates and having draw-off cocks at different levels. The essential features of the process[1] are as follows. The argon is carried towards the base of the column by the colder liquids descending from the upper plates; on the other hand it is carried upwards by the ascending gaseous oxygen evaporated from the liquid oxygen bath at the base of the column. As a result argon accumulates on the lower plates of the column. When its partial pressure over these plates reaches a certain magnitude its concentration will cease. At this stage the argon escapes with the separated nitrogen and oxygen to such an extent as to counterbalance the fresh quantities introduced by the liquid air. Gas containing up to 10% of argon and very little nitrogen can thus be withdrawn from above a suitable plate. This gas is rectified in a separate column, the latter being furnished with a condenser at its summit, cooled by a suitable refrigerant such as liquid nitrogen boiling at approximately atmospheric pressure. The gas mixture withdrawn from the top of the second column contains about 70% of argon, under 1% of nitrogen, and the balance oxygen. The oxygen in this mixture is removed by a suitable chemical method, *e.g.* combustion with hydrogen.

Data on the evaporation of oxygen-nitrogen-argon mixtures are given by Rayleigh (Phil. Mag. 1903 [vi], **5**, 677), Inglis (Phil. Mag. 1906 [vi], **11**, 640), Holst and Hamburger (Z. phys. Chem. 1916, **91**, 513), and Fonda, Reynolds, and Robinson (Ind. Eng. Chem. 1925, **17**, 676). For a bibliography of the technical production of argon from liquid oxygen and by the fractionation of liquid air, *see* Abegg's "Handbuch," Vol. 4, p. 472, 1928, "Die Edelgase," by E. Rabinowitsch.

The production of argon from argon-nitrogen mixtures by adding hydrogen, forming ammonia by means of a suitable catalyst, and subsequently removing hydrogen with copper oxide, has been proposed (U.S.P. 1658631; *see also* B.P. 358842; Helv. Chim. Acta, 1928, **11**, 761). The purge gas from ammonia synthesis has the approximate composition H_2 65%, N_2 30%, $A > 3\%$, and $O_2 > 1\%$, and has been suggested as a source of argon (U.S.P. 1892186, 1933).

Separation of Argon from the other Rare Gases.—Argon prepared from the atmosphere by chemical absorption of oxygen and nitrogen is always contaminated with the other rare gases. Even when liquid air is rectified the other rare gases are never completely removed. Their presence does not in general interfere with the use of argon in the lamp industry.

Chemically pure argon has been prepared by a process of fractional condensation and evaporation at low temperatures (Ramsay and Travers, Proc. Roy. Soc. 1899, **64**, 183; 1900, **67**, 329; Ewers, Ann. Phys. 1905 [4], **17**, 804; Moles, Ber. 1927, **60**, 134). Fractional adsorption may also be used in separating the rare gases from one another When a mixture of these gases is passed over charcoal cooled in liquid air helium and neon are not adsorbed, whereas argon, krypton, and xenon are retained quantitatively. On raising the temperature to −80° pure argon is evolved and krypton and xenon are retained (Liveing and Dewar, Proc. Roy. Soc. 1901, **68**, 390; Dewar, Proc. Roy. Soc. 1904, **74**, 127).

Density and Atomic Weight of Argon.—The density of argon has been determined by a number of observers. The following values for the molecular weight may be quoted: 39·95 (Van Laar, J. Chim. phys. 1919, **17**, 266); 39·94 (Moles, Ber. 1927, **60**, 134); 39·944 (Baxter and Starkweather, Proc. Nat. Acad. Sci. 1928, **14**, 57; 1929, **15**, 441). The monatomic nature of the argon molecule is proved by the ratio of the specific heat at constant pressure to that at constant volume, which is 1·65 according to Rayleigh and Ramsay (Proc. Roy. Soc. 1895, **57**, 265; *see also* Ramsay, Phil. Trans. 1895, A, **186**, 237; Strieder, Verh. Deuts. Phys. Ges. 1914 [2], **16**, 615 (1·669); Dixon, Campbell, and Parker, Proc. Roy. Soc. 1921, A, **100**, 1 (1·676)).

Physical Data.—Argon has three isotopes of masses 40, 38, and 36, which are present in the proportions of 99·62%, 0·05%, and 0·33% respectively. Disintegration of the nucleus by bombardment with α-particles was observed by Rutherford and Chadwick (Proc. Phys. Soc. 1924, **36**, 417). In its extra-nuclear structure argon has 2 1*s*, 2 2*s*, 6 2*p*, 2 3*s*, and 6 3*p* electrons. The outer shell thus has a complete octet.

Solid argon is optically isotropic. At the temperature of liquid hydrogen it gives a cubic face-centred lattice (a 5·42±0·02Å) (Simon and Simson, Z. Physik, 1924, **25**, 160).

Argon is a colourless gas condensing to a colourless liquid of boiling-point −185·84° and melting-point −189·30° (Crommelin). The density of liquid argon is tabulated below:

−183·15°	−161·23°	−140·20°	−131·54°
1·37396	1·22414	1·03456	0·91499

(Mathias, Kammerlingh Onnes, and Crommelin, Akad. Amsterdam Versl. 1911, **19**, 394). The atomic volume of the liquid at its boiling-point is 28·4. Although the gas is monatomic it is considered by some authors that liquid argon is associated (*cf.* Dolezalek, Z. phys. Chem. 1918, **93**, 585; Muller, Compt. rend. 1922, **175**, 760).

Isotherms of argon have been measured by Ramsay (Phil. Trans. 1895, A, **186**, 237), Ramsay and Travers (Proc. Roy. Soc. 1898, **64**, 183), Holborn and Schultze (Ann. Phys. 1915 [4], **47**, 1089), and Bridgeman (Proc. Nat. Acad. Washington, 1923, **9**, 370). Tanner and Masson (Proc. Roy. Soc., A, 1930, **126**, 268) have measured the compressibility of argon and of argon-hydrogen mixtures up to 125 atm. Holborn and Schultze give the compressibility coefficient as −0·00091. Values of the expansion coefficient between −100° and 400° are tabulated by Holborn and Otto (Z. Physik, 1924, **23**, 90; 1924, **30**, 325). The critical temperature is −122·44, the critical pressure is 47·996 atm., and the critical density is given by Crommelin as 0·509 (Gmelin-Kraut, 8th ed., "Edelgase," 1926, i, 143).

Vapour Pressure of Argon (data from Landolt-Börnstein Tabellen):

Temp. (° Abs.)	67·77	72·12	77·49	83·78	87·77
V.p. (mm.)	38·3	84·56	208·8	518·7	802·0

---

[1] We are indebted to Dr. C. R. Houseman of the British Oxygen Company, Ltd., for this information.

The vapour pressure of the liquid is represented by the formula log $p=4{\cdot}85033-634{\cdot}391T+30769{\cdot}09T^2-1076464T^3$. For solid argon the observations are best expressed by the formula log $p=A/T+BT+D$ log $T+C$, in which $A=+9034{\cdot}32$, $B=-1{\cdot}42112$, $C=-1014{\cdot}0278$, and $D=+533{\cdot}0275$ (*see also* Gmelin-Kraut, *l.c.*).

The melting-point of argon is −189·3° (Crommelin, Akad. Amsterdam Versl. 1914, **22**, 1212). For its dependence on pressure, *see* Ruhemann, Simon, and Edwards (Z. physikal. Chem., B, 1930, **6**, 331 ; **7**, 80) ; Bridgman (Phys. Rev. 1934 [2]), **46**, 930). The heat of vaporisation near the boiling-point is 37·6 g.-cal., while the heat of fusion is 6·7 g.-cal. (Eucken, Verh. phys. Ges. 1916, **18**, 16). The same author has determined the specific heat of solid and of liquid argon at 17·8°–93·9° Abs. The true chemical constant of argon is 0·79±0·04. Weber (Ann. Phys. 1917 [4], **54**, 437) found the thermal conductivity at 0° to be 385×10^{-7} cal./cm. sec. degree. The accommodation coefficient on platinum is 0·852 (Knudsen, Ann. Phys. 1915 [4], **46**, 641) at 30°–260°.

Surface Tension (Rudorf, Ann. Phys. 1909 [4], **29**, 751) :

T (° Abs.) . .	84	86	88	90
γ in dynes per cm.	13·45	12·93	12·42	11·91

The viscosity of argon at 0° is 2114×10^{-7} dyn. sec./cm.^{2} (Schierloh, Diss. Halle, 1908). Trautz, Binkele, and Zink (Ann. Phys. 1930 [5], **5**, 561 ; [5], **7**, 427) have obtained data for temperatures from 20° to 827°, and have studied mixtures with He, Ne, and H_2. The viscosity of liquid argon was measured by Rudenko and Schubnikov (Physikal. Z. Sovietunion, 1934, **6**, 470 ; A. 1935, 1064).

Diffusion of Argon.—Argon will not diffuse through red-hot iron, palladium, or platinum (Ramsay and Travers, Proc. Roy. Soc. 1897, **61**, 267). It will pass through rubber more rapidly than does N. Edward and Pickering (Chem. Met. Eng. 1920, **23**, 17, 71) found that the rate of diffusion of argon through rubber is proportional to the partial pressure. Its value, relative to H=1, is 0·26.

Solubility.—The solubility of argon in water at 12° is 3·94 vols. per 100 vols. of water (Rayleigh and Ramsay, Phil. Trans. 1895, A, **186**, 187). The Bunsen absorption coefficient, β', in water has the following values at 0°–50° (Estreicher, Z. phys. Chem. 1899, **31**, 176):

Temp.	β'	Temp.	β'	Temp.	β'
0	0·05780	15	0·04099	35	0·03053
1	0·05612	20	0·03790	40	0·02865
5	0·05080	25	0·03470	45	0·02731
10	0·04525	30	0·03256	50	0·02567

Values of the Bunsen coefficient for argon in water, methyl alcohol, ethyl alcohol, acetone, benzene, and *cyclo*hexane (at 15°) are 0·0371, 0·253, 0·243, 0·271, 0·220, 0·308 (Lannung, J. Amer. Chem. Soc. 1930, **52**, 68 ; *see also* Sisskind and Kasarnowsky, Z. anorg. Chem. 1931, **200**, 282 ; *ibid.* 1933, **214**, 385). The solubility of argon in salt solutions was studied by Åkerlöf (J. Amer. Chem. Soc. 1935, **57**, 1196).

Sorption of Argon.—Argon is absorbed by certain metals. Soddy and Mackenzie observed the absorption of the gas by aluminium electrodes (Proc. Roy. Soc. 1907, A, **80**, 94), and a heated tungsten wire will also absorb it (Langmuir, J. Amer. Chem. Soc. 1915, **37**, 1140). It is absorbed less by sputtered platinum than are helium and other gases. Langmuir found that argon was absorbed by glass at −118° to −183° (J. Amer. Chem. Soc. 1917, **39**, 1848; 1918, **40**, 1361).

1 c.c. of freshly ignited cocoanut charcoal at 0° will absorb 12 c.c. and at −185° 175 c.c. of argon. The heat evolved in this process at −185° is 25·0 g.-cal. (Dewar, Proc. Roy. Soc. 1904, A, **74**, 122). The temperature variation of the absorption by charcoal has been studied by Homfray (Proc. Roy. Soc. 1910, A, **84**, 99). The absorption of the rare gases by chabasite is quantitatively of the same order as that by charcoal (Seeliger and Lapkamp, Physikal. Z. 1921, **22**, 563 ; Baxter and Starkweather, Proc. Acad. Washington, 1925, **11**, 231 ; 1926, **12**, 20).

The refractive index of argon against air is 1·0002796 for λ 6439 Å and 1·0002852 for λ 4359 Å (Cuthbertson, Proc. Roy. Soc. 1910, A, **84**, 13 ; *see also* Rusch, Ann. Phys. 1923 [4], **70**, 373 ; Quarder, *ibid.* 1924 [4], **74**, 255).

The discharge through argon in a Geissler tube at a pressure of 3 mm. is red in colour. This changes to steel blue on reducing the pressure and introducing capacity into the circuit. An intense discharge in argon at a higher pressure has an almost white colour. The nature of the discharge varies with the tube dimensions, pressure, etc. The principal lines in the red (arc) spectrum of argon are :

λ	Intensity.	λ	Intensity.
4044·42 Å	8	4300·10 Å	8
4158·59 ,,	9	4333·56 ,,	6
4164·18 ,,	7	4335·29 ,,	6
4181·88 ,,	7	4345·17 ,,	7
4191·03 ,,	8	4510·73 ,,	8
4198·31 ,,	8	6032·13 ,,	7
4200·88 ,,	9	6416·31 ,,	6
4259·36 ,,	9	6965·43 ,,	6
4266·28 ,,	8	7067·22 ,,	5
4272·17 ,,	8		

The chief lines in the visible part of the blue (spark) spectrum of argon are tabulated below :

λ	Intensity.	λ	Intensity.
3588·49 Å	9	4277·5 Å	8
3729·33 ,,	9	4348·0 ,,	10
3841·52 ,,	8	4426·0 ,,	8
3850·56 ,,	9	4806·0 ,,	8
3928·61 ,,	8	5305·8 ,,	8
4103·9 ,,	9		

(*see* Kayser, " Handbuch d. Spektroskopie," Springer, Berlin ; *also* Landolt-Börnstein

Tabellen, III Ergänzungsband, ii, 795 ; Meissner, Z. Physik, 1926, **39**, 172 ; **40**, 839).

Argon is feebly diamagnetic, its volume susceptibility at 0° and 1 atmosphere being $-0{\cdot}00953 \times 10^{-6}$ abs. units (Tänzler, Ann. Phys. 1908 [4], **24**, 931). Lehrer (Z. Physik, 1926, **37**, 155) obtained a value of $-0{\cdot}00088 \times 10^{-6}$. The lower figure is more probable on theoretical grounds. The dielectric constant (0°, 760 mm.) is 1·000555. The molecular diameter calculated from the dielectric constant is $2{\cdot}36 \times 10^{-8}$ cm. Values obtained by other methods vary from $3{\cdot}69 \times 10^{-8}$ to $1{\cdot}70 \times 10^{-8}$ cm.

Less than 1% of nitrogen may be detected spectroscopically in argon, but much larger amounts of argon must be present in nitrogen before the characteristic line spectrum of the former is observed. The limits of detection by visual spectroscopy, according to Collie and Ramsay (Proc. Roy. Soc. 1896, **59**, 257) are: 0·06% of **A** in presence of **He**; 37% of **A** in presence of N_2 ; 2·5% of **A** in presence of O_2. 25% of **He** can just be detected spectroscopically in argon at a pressure of 0·015 mm. ; 0·08% of N_2 cannot be detected in argon at total pressures below 1 mm. Krypton and xenon may be detected when present in argon to the extent of only 0·015 and 0·02% respectively. These values depend on the discharge conditions to a considerable extent.

Compounds of Argon.—Villard (Compt. rend. 1896, **123**, 377) obtained a hydrate of argon by compressing the gas to 150 atmospheres at 0° in presence of ice. De Forcrand (Compt. rend. 1902, **135**, 959 ; Ann. Chim. Phys. 1903 [7], **29**, 46) found its dissociation pressure at +0·2° to be 98·5 atmospheres. The formula of the hydrate is $A,5{\cdot}5H_2O$ (*see also* Tammann and Krige, Z. anorg. Chem. 1925, **146**, 179).

Compounds of boron trifluoride and argon have been prepared recently by Booth and Willson (J. Amer. Chem. Soc. 1935, **57**, 2273). The graph of freezing-point against composition in the system BF_3—**A** gave a series of maxima and minima. The maxima corresponded to the ratios A, BF_3 ; $A, 2BF_3$; $A, 3BF_3$; $A, 6BF_3$; $A, 8BF_3$; and $A, 16BF_3$; indicating the formation of compounds with these formulæ. They are unstable, however, and dissociate above their melting-points. It was suggested that the argon atom functions as a donor of electrons in forming these substances.

Many unsuccessful attempts have been made to induce argon to enter into normal chemical combination. Thus Moissan (Proc. Roy. Soc. 1895, A, **58**, 120 ; Compt. rend. 1895, **120**, 966) heated argon with lithium, boron, titanium, and uranium. Fischer and his co-workers attempted to prepare argon compounds in the electric arc (Ber. 1908, **41**, 3802, 4449 ; 1909, **42**, 527 ; 1910, **43**, 1442, 1453 ; *see also* Rayleigh and Ramsay, Phil. Trans. 1895, A, **186**, 187 ; Ramsay and Collie, Proc. Roy. Soc. 1897, **60**, 53 ; Matignon, Compt. rend. 1900, **131**, 837). The so-called "clean-up" of the rare gases in an electrical discharge is believed to be due to adsorption by the sputtered electrode material, rather than to actual compound formation. (For bibliography, *see* Abegg's "Handbuch," vol. 4, p. 486, "Die Edelgase," by E. Rabinowitsch.)

Determination of Argon.—The determination of argon when it is mixed with reactive gases such as nitrogen, oxygen, or hydrogen consists essentially in removing the reactive gases by chemical means and measuring the volume of the residue. Determinations of this type are described by Ruff and Hartmann (Z. anorg. Chem. 1922, **121**, 167). Calcium may conveniently be used as an adsorbent for nitrogen in nitrogen-argon mixtures. Moureu (Compt. rend. 1906, **142**, 44) used a mixture of lime and magnesium as an adsorbent in measuring the argon content of natural gases. The sparking method has also been used for removing nitrogen quantitatively. Holst and Hamburger absorbed nitrogen from nitrogen-argon mixtures by means of a discharge in potassium vapour at 200° (Z. physikal. Chem. 1916, **91**, 513). These authors also used the density for measuring the composition of nitrogen-argon mixtures.

The index of refraction of mixtures of argon and nitrogen was used as a basis for analysis by Hamburger and Filippo (Z. angew. Chem. 1914, **28**, 75). Skaupy and Bobek used a similar method in analysing helium-argon mixtures (Z. techn. Physik. 1925, **6**, 284). Moureu and Lepape (Compt. rend. 1911, **152**, 691) developed a spectrophotometric method of determining the krypton and xenon contents of argon which depends on intensity measurements of certain lines in the visible spectra of the three gases and comparison with measurements on standard mixtures. Argon may be determined in mixtures with helium and neon by adsorption in charcoal (*see also* Pascal, Traité de Chimie Minerale, 1934, vol. 12, 140 ; Copaux, Bull. Soc. chim. 1932 [iv], **51**, 989–992). Van Liempt and Visser (Rec. trav. chim. 1934, **53**, 1084) describe a spectrographic method of detection of argon in argon-nitrogen mixtures. Gerling (J. Appl. Chem. Russ. 1933, **6**, 1153 ; A. 1934, 269) has developed a method for estimating argon and helium in natural gases which is based on measurements of the thermal conductivity of the rare gas mixture.

Uses of Argon.—Argon has been used in filling vapour-pressure thermometers for use at 60° to 90° Abs. (Born, Ann. Phys. 1922 [4], **69**, 473). The chief technical use of argon is for filling the so-called "gas-filled" electric lamps. In pure argon there is a risk of arc formation and a mixture of argon with 15% of nitrogen is generally employed.

Discharge tubes containing argon have a low luminous efficiency, and sputtering of the electrode material is usually more pronounced in argon than in the other rare gases. Argon may be used in conjunction with mercury in the production of blue and green tubes.

H. J. E.

ARGONIN. Trade name for a preparation of silver caseinate. Its aqueous solution is not precipitated by chlorides. Local antiseptic.

ARGULAN. Dimethylphenylpyrazolone mercury sulphaminate. Introduced as an antiluetic.

ARGYRODITE. A sulpho-germaniate of silver, being the mineral in which the element germanium was discovered in 1886. It had, however, been mentioned by A. Breithaupt in 1823, under the name *Plusinglanz*. These occurrences in the Himmelsfürst silver-mine at Freiberg, Saxony, show only botryoidal crusts with a minutely crystallised surface. Later, the mineral was found as distinct, though small, cubic crystals in Bolivia, analysis of which proved the formula to be Ag_8GeS_6 (S. L. Penfield, 1893 and 1894). More recently, cubic crystals of larger size (3·5 cm. across; sp.gr. 6·235) from Colquechaca, Bolivia, have been described and analysed (V. M. Goldschmidt, Z. Kryst. Min. 1908, **45**, 548). At this locality the mineral appears to be not uncommon, and no doubt large quantities of it have been smelted for silver. In external appearance it is not unlike but is less sectile than argentite.

In the Bolivian mineral the germanium may be replaced isomorphously by tin, giving the species *canfieldite*, Ag_8SnS_6 (Penfield, 1894). Intermediate members of this series, or stanniferous argyrodite, also occur at Colquechaca, Bolivia (Prior and Spencer, 1898). L. J. S.

ARGYROL. Trade name for colloidal silver. Antiseptic.

ARHÉOL. Trade name for *santalol*, $C_{15}H_{23}{\cdot}OH$, the chief constituent of East Indian sandalwood oil.

ARHOIN. Trade name for an addition product of diphenylamine and ethylthymylbenzoate.

ARIBINE. An alkaloid from the bark of the Brazilian tree *Arariba rubra* (Rieth and Wöhler, Annalen, 1861, **120**, 274), is identical with *harman*, $C_{12}H_{10}N_2$ (Spath, Monatsh. 1919, **40**, 351); *v.* HARMALA ALKALOIDS. G. B.

ARICINE *v.* CINCHONA ALKALOIDS.

ARISTIDINIC ACID *v.* ARISTOLOCHINE.

ARISTINIC ACID, $C_{18}H_{13}O_7N$, greenish-yellow needles, m.p. 275° (decomp.). Occurs with *aristidinic acid*, $C_{18}H_{13}O_7N$, m.p. 260°, and *aristolic acid*, $C_{15}H_{11}O_7N$ or $C_{15}H_{13}O_7N$, m.p. 260°–270°, in *Aristolochia argentina* (Griseb.) (Hesse, Arch. Pharm. 1895, **233**, 684).

ARISTOCHIN or ARISTOQUININE. Trade name for di-quinine carbonate, $CO(O{\cdot}C_{20}H_{23}N_2O)_2$.

ARISTOL. Trade name for di-iododithymol, used as a substitute for iodoform.

ARISTOLOCHIC ACID, from *Aristolochia clematitis*, *A. longa* and *A. rotundifolia* is identical with Pohl's aristolochine (Castille, J. Pharm. Belg. 1922, **4**, 569).

ARISTOLOCHINE, $C_{17}H_{11}O_7N$ (or $C_{32}H_{22}O_{13}N_2$?), orange-yellow needles, decomposing at 215°. Occurs in *Aristolochia clematitis* (Linn.) and *A. rotunda* (Linn.). It is a weakly acid base (Pohl, Arch. expt. Path. Pharm. 1891, **29**, 282). According to Hesse (Arch. Pharm. 1895, **233**, 684) aristolochine is a homologue of aristolic acid (*see* under ARISTINIC ACID). The alkaloid is highly toxic. G. B.

ARNICA MONTANA, ARNICA FLOWERS, ARNICA ROOT. The flowers of a small perennial found in Central Europe contain the yellow crystalline arnicin, the colourless crystalline phytosterol, arnisterol, and a volatile oil. The rhizome forms the drug, arnica root; it also contains arnicin and a volatile pungent oil.

The tincture of each drug is used for sprains and bruises (B.P.C. 1934, 158).

ARNICA YELLOW *v.* DYESTUFFS, AZO.

ARNICIN *v.* ARNICA MONTANA.

ARNISTEROL *v.* ARNICA MONTANA.

AROMADENDRENE. This hydrocarbon, $C_{15}H_{24}$, b.p. 121°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·9116, $n_D^{20^\circ}$ 1·4978, $[\alpha]_{577}^{20^\circ}$ − 6·1°, is stated to be the main sesquiterpene constituent of eucalyptus oils (Baker and Smith, "A Research on the Eucalypts," 1920, p. 416). It yields no crystalline derivatives and according to Briggs and Short (J.C.S. 1928, 2524) it is tricyclic, giving on oxidation a ketone, *aromadendrone*, $C_{14}H_{22}O$, m.p. 80°–81°. J. L. S.

AROMADENDRONE *v.* AROMADENDRENE.

AROMATIC HYDROCARBONS, OCCURRENCE IN PETROLEUM. All crude petroleums contain more or less of the benzenoid series of hydrocarbons, some to a relatively small extent, as, for example, the so-called paraffinoid crudes of Pennsylvania, and some to a very considerable extent. For example, in the Koetei field of Borneo the petrol fraction contains upwards of 40% of this series, and actually was widely used during the World War as a source of toluene for the preparation of *Trotyl* (TNT) (J. Inst. Petroleum Tech. 1921, **7**, 215). Other crudes containing aromatic hydrocarbons are derived from Ohio, Burma, Rumania, Iran, and Oklahoma.

The substances in this series that have been characterised are benzene, toluene, *o*-, *m*-, and *p*-xylene (it is interesting to note that the *m*-xylene is the predominating member), mesitylene and *pseudo*cumene, naphthalene (Mabery, J.S.C.I. 1900, **19**, 502), and alkylnaphthalenes (Jones and Wooton, J.C.S. 1907, **91**, 1146).

The highest fractions, namely, the lubricating oils derived from petroleum, also contain traces of aromatic hydrocarbons. Brooks, for example, has ascribed the fluorescence of these fractions to aromatic material which has yielded traces of crystalline picrates (private communication).

Extraction of Aromatic Hydrocarbons.—Aromatic hydrocarbons may be also obtained by the heat treatment or pyrolysis of the lower paraffins and olefines, and further some concentration of these hydrocarbons can be achieved by the application of a selective solvent to the various fractions of petroleum. It is due to the Rumanian chemist Edeleanu that this method of extraction was first made possible. The removal of aromatic hydrocarbons from the kerosine fractions, whereby a general improvement in the burning properties of the oil is brought about, also serves as a source of an aromatic concentrate which can be made use of in increasing the anti-knock characteristics of a paraffinoid motor spirit.

Pyrolysis.—A summary of the pyrolysis or thermal treatment of gaseous hydrocarbons is given by Dunstan, Hague, and Wheeler (Ind. Eng. Chem. 1934, **26**, 307). The hydrocarbon gases under question are passed through a heated tube system and the aromatic hydrocarbons produced are separated from the issuing gases by ordinary conventional methods of adsorption.

The following tables show the yields obtained when the simple paraffins and olefines are treated :

TABLE 1.

PYROLYSIS AT ATMOSPHERIC PRESSURE OF THE PARAFFIN HYDROCARBONS FOR THE PRODUCTION OF AROMATIC HYDROCARBONS.

Gas.	Temp. °C.	Conversion into liquids (% by weight).	Conversion into distillate boiling below 170°C %	Gallons per 1,000 cu. ft. total oils.	Gallons per 1,000 cu. ft. distillate boiling below 170°C.
Methane	1050	8·8	5·0	0·44	0·25
Ethane	850	17·93	11·2	1·7	1·1
	900	21·9	10·63	2·1	1·0
Propane	850	23·09	11·65	3·25	1·6
Butane	800	20·4	12·91	4·0	2·4
	850	24·55	11·64	4·6	2·35
Pentane	850	26·8	11·87	—	—
Hexane	800	33·7	19·2	—	-
	850	33·8	19·0	—	-

TABLE 2.

PYROLYSIS AT ATMOSPHERIC PRESSURE OF THE OLEFINE HYDROCARBONS FOR THE PRODUCTION OF AROMATICS.

Gas.	Temp. °C.	Conversion into liquids (% by weight).	Conversion into distillate (% by weight).	Gallons per 1,000 cu. ft total oils.	Gallons per 1,000 cu ft. distillate.
Ethylene	800	36·1	17·7	3·15	1·6
Propylene	750	35·6	20·4	4·7	2·75
	800	40·6	19·0	5·32	2·5
Δ^{α}-Butylene . . .	700	35·8	23·6	6·25	4·1
	750	39·6	22·45	6·85	3·95
Δ^{β}-Butylene . . .	700	37·0	25·8	6·4	4·45
	750	39·6	23·2	6·85	4·1

It is of interest to note that the aromatic hydrocarbons produced are a mixture of benzene, toluene, the xylenes, styrene, indene, naphthalene, alkyl naphthalene, anthracene and phenanthrene.

Alternatively, it is possible to operate under somewhat easier temperature conditions by first bringing about dehydrogenation of the paraffin and then pyrolysing the olefines thus produced.

Wheeler's explanation of the mechanism of the operation assumes that ethylene is the starting-out material, this readily polymerises to butylene, butylene by dehydrogenation produces butadiene, butadiene and ethylene unite to give *cyclo*hexene, and *cyclo*hexene in turn produces benzene. In this connection it may be noted that in the familiar cracking operation carried out for the production of motor fuel from heavy hydrocarbons the C_4 fraction invariably contains considerable quantities of butadiene.

Practical Application of Aromatic Hydrocarbons from Petroleum.—The utilisation of the benzene series for improving the anti-knock qualities of petrol is well known, and the above procedure leads to this end.

References have been made to the application of Borneo spirit in the manufacture of trotyl, and it is therefore of importance to realise that vast quantities of aromatic hydrocarbons are potentially obtainable from the waste gases of the petroleum industry. A. E. D.

ARRACK (*Arack* and *Rack*, Fr. ; *Arrack Reisbranntwein*, Ger.). The term is derived from araq or arak, which was generally applied by the Arabs to all distilled spirits but is now usually restricted to the alcoholic liquor obtained by distillation of the fermented juice of the cocoanut palm (toddy or palm wine) or from rice or a mixture of both. Arrack is also made from the succulent flowers of the Bassia genus of trees and from other vegetable products in the West Indies. In Germany a spirituous liquor prepared from molasses, rice, and barley offal is sold as arrack and is stated by Kurt Brauer (Chem.-Ztg. 1923, **47**, 365, 370) to be similar in composition. When rice is used it is steeped in water in large vats and agitated cautiously (so as not to damage the grains and thus interfere with subsequent fermentation) until about half the rice has begun to germinate. The water is then run off from below, and toddy or molasses or a mixture of these is added to the rice. The whole is allowed to ferment and the mixture is then distilled. This method, which is said to produce the best quality of arrack, obtains at Batavia and in Jamaica, but in India arrack is frequently made from toddy alone.

The best quality arrack is agreeable to the taste, but some poor qualities made in the East have a somewhat nauseous odour and taste, due to a volatile oil which distils from the rice and is narcotic and very unwholesome. In some of the inferior products of the East also the intoxicating effect is frequently increased by the addition of hemp leaves, poppy heads, stramonium juice, etc. An imitation arrack is sometimes made by flavouring rum with flowers of benjamin or benzoic acid. Weistenfeld and Luckow (Z. Unters. Lebensm. 1931, **61**, 465), in examining twenty-three samples, found that the alcoholic content was about 58% by volume, whilst the esters varied from 230 to 470 mg. per 100 ml. of alcohol.

A large amount of revenue is obtained from the manufacture of arrack in Siam and Ceylon, and the latter exports a considerable quantity to the United Kingdom, where it is used in the mixing of punch and "cocktails."

F. G. H. T.

ARRAPO *v.* BASSIA FATS.

ARRHENAL *v.* ARSENICALS, ORGANIC; ALIPHATIC ARSENICALS.

ARRONAL *v.* ALLOYS, LIGHT.

ARROWROOT is the starch obtained from the rhizomes of *Maranta arundinacea*, which is indigenous to tropical America. The manufacture of arrowroot is largely centred in St. Vincent.

The roots are stripped of external covering, pulped, strained, and the starch is removed and purified by prolonged washing.

The rhizomes reach their maximum yield in about 12 months, starch formation being particularly rapid during the final 4 months. Other starches sold under the name of "arrowroot" include that from *Canna edulis* ("Tous-les-mois" or Queensland arrowroot), from cassava (Brazilian arrowroot), and from the yam (British Guiana arrowroot). Samples of true arrowroot from St. Vincent have been found to contain "marble" arrowroot derived from *Myrosma cannifolia*, another member of the same family of plants sometimes found growing with Maranta.

The various "arrowroots" may readily be distinguished microscopically.

The Maranta root gives the following analysis:

Water	Starch	(Dextrin + Sugar)
63·4	27·8	2·1

Fibre	Ether extract	Protein	Ash
3·9	0·2	1·6	0·9

The prepared arrowroot is one of the purest natural carbohydrates. Jones (Food, 1933, **3**, 87) gives the following analysis:

Water	Protein	Fat	Starch	Fibre	Ash
15·00	0·01	0·02	84·67	0·03	0·18

25–30% of starch is obtained from the whole roots. The value of arrowroot in sickroom dietary is attributable to its purity, to its high gelatinising point (73°C.) with which is associated high digestibility, and to its ability to prevent the coarse curdling of milk.

A. G. Po.

ARSACETIN, Acetyl Atoxyl=sodium acetyl-*p*-arsanilite, *v.* ARSENICALS, ORGANIC.

ARSAMIN, Atoxyl, sodium *p*-arsanilate, *v.* ARSENICALS, ORGANIC.

ARSAMINAL. Japanese name for salvarsan.

ARSENIC, sym. **As**, at. wt. 74·91, at. no. 33; no isotope indicated.

History.—The arsenic sulphides realgar and orpiment were known to the Greeks and in the first century A.D. the name arsenicum was applied to orpiment. White arsenic (arsenious oxide) was described in the fifth century. Geber and Albertus Magnus believed that arsenicum contained a metal. N. Lemery prepared metallic arsenic by heating white arsenic with soap and potash (1675). Brandt recognised white arsenic as the calx, in modern terms the oxide of arsenic (1773). Finally Berzelius determined the equivalent weights of arsenic and arsenious oxide (1817).

Occurrence.—In small quantities arsenic is one of the most widely-distributed elements. Igneous rocks contain about 0·007%, sea-water 0·025 mg. per litre near the surface and 0·08 mg. at a depth of about 6,000 metres. A. C. Chapman found 0·33 mg. As_2O_3 in the Thames estuary as an average figure. Mineral waters, river sands, and meteoric iron contain traces of arsenic. From the rocks arsenic passes into the soil and thence into the tissues of plants and animals. Soil may contain from 1 to 60 parts per million, and fresh vegetables 0·05 part. The adult human body contains about 0·1 mg. **As** per kg. weight (Billeter and Marfurt, Helv. Chim. Acta, 1923, **6**, 780). American tobacco may contain 6 to 30 parts per million (Remington, J. Amer. Chem. Soc. 1927, **49**, 1410). Oysters and marine fish contain from 3 to 4 parts of arsenic per million, but A. C. Chapman (Analyst, 1926, **51**, 548) found from 10 to 119 parts As_2O_3 in the fresh edible parts of shellfish. One-hundredth of a grain of arsenic, As_2O_3, per lb. (1·4 parts per million) is the legal limit for drugs and also the maximum permitted by the Ministry of Health for apples, a regulation due to the use of arsenical sprays. Paris green, lead arsenate, and calcium arsenate are largely used for this purpose (Annual Survey of American Chemistry, 1933, **8**, 222). Since arsenic occurs in pyritic minerals and in native sulphur, it may pass into sulphuric acid and thence into a large number of chemicals and manufactured articles. The epidemic of arsenical poisoning in the North of England in 1900 was traced to beer containing arsenic derived from glucose manufactured from starch with sulphuric acid containing arsenic (*see* Royal Commission Report on Arsenical Poisoning, 1903). Arsenic, if present in the sulphur dioxide generated for the contact process of sulphuric acid manufacture, would "poison" a platinum catalyst, the gases are therefore purified from arsenic compounds and the contact acid is free from arsenic. Pigments containing arsenic as an essential constituent are *Scheele's green*, $CuHAsO_3$, and *Schweinfurt's green*,

$$Cu(AsO_2)_2{\cdot}Cu(C_2H_3O_2)_2,$$

formerly used for colouring wall-paper; they have caused poisoning either from the dust of the pigment or by the action of mould growths liberating the poisonous gas trimethylarsine, $As(CH_3)_3$ (Challenger, Higginbottom, and Ellis, J.C.S. 1933, 95).

Minerals and Sources.—Arsenic combined with sulphur is found as *realgar*, AsS (*q.v.*), in Hungary, Saxony, Switzerland, and China, and as *orpiment*, As_2S_3 (*q.v.*), in Hungary and the Hartz. Other sulphide ores include *mispickel* (*q.v.*), *arsenical pyrites* or *white mundic*, $FeS_2{\cdot}FeAs_2$; *cobaltite*, $CoAsS$ (*q.v.*) ; *gersdorffite* (*q.v.*) or *nickel glance*, $NiAsS$; it also occurs as *erythrite* (*q.v.*) or *cobalt bloom*, a hydrated cobalt arsenate, $Co_3(AsO_4)_2{\cdot}8H_2O$, and as arsenates and arsenites of iron, copper, lead, zinc, etc. As arsenide, it is found combined with iron, as *löllingite* (*q.v.*) or *leucopyrite*, $FeAs_2$, and minerals of the formulæ Fe_2As_3 and Fe_3As_4 ; with nickel, as *niccolite* (*q.v.*), *nikeline* or *kupfernickel*, $NiAs$, and as *chloanthite*, $NiAs_2$ (*q.v.*) ; with cobalt, as *smaltite* (*q.v.*) or *tin white cobalt*, $Co(NiFe)As_2$. Less important minerals are native arsenic, which contains varying quantities of antimony, iron, nickel, and other metals, and two forms of arsenious oxide, the isometric *arsenolite* and the monoclinic *claudetite*.

The world's supply of arsenic is now recovered almost entirely as a by-product from the flue dusts of various smelters, especially those of copper, lead, and tin. The United States of America and Mexico have become large producers and these together with Sweden account for most of the arsenic recovered. Sweden, which produced very little arsenic prior to 1926, has since then become the most important producing country in the world (*cf.* Mineral Industry, 1934, **43**, 43).

Preparation.—Metallic arsenic is used only to a small extent. It is usually prepared from native arsenic, löllingite, or mispickel. The mineral is heated in the absence of air in earthenware retorts or tubes laid horizontally in a long furnace. Great care is required in manufacturing the retorts, which must be strong, heat-resisting and quite impervious to the vapour of arsenic. A piece of thin iron sheet is rolled and inserted into the mouth of the retort, and an earthenware receiver luted on. During the distillation less than half of the arsenic is volatilised and condenses on the iron as a nearly white, coherent, internally crystalline mass which, after cooling, is detached by unrolling the iron. If necessary the arsenic is purified by redistillation and the residues are burnt and the volatile product, arsenious oxide, is recovered. Arsenious oxide is sometimes heated with charcoal in an earthenware crucible covered with an inverted crucible or with a conical iron cap. The metallic arsenic thus produced is grey and pulverulent and always contains arsenious oxide. Arsenic may also be prepared by heating the sulphide ores with charcoal and sodium carbonate, or with potassium cyanide. Pure arsenic has been prepared from ammonium hydrogen arsenate, $(NH_4)H_2AsO_4$, by heating this salt to 1,000° in a current of ammonia, the arsenic thus obtained is redistilled in vacuo (de Passillé, Compt. rend. 1934, **198**, 1781).

Properties.—Commercial arsenic is a very brittle steel-grey metalline mass of sp.gr. 5·73 of brilliant lustre, which becomes dull on exposure to air. It crystallises in rhombohedra isomorphous with metallic antimony and bismuth. It is a conductor of electricity and is odourless and tasteless.

There are four allotropic forms of arsenic, the ordinary metallic α-form having properties given above, a grey β-form, a yellow γ-form, and a brown amorphous form.

The grey, vitreous, or β-form of arsenic is produced when the vapour is condensed on a cool surface at 210°–220° or in an atmosphere other than arsenic such as hydrogen. This form has a sp.gr. of 4·71 ; on heating to 360° it is converted into the α-form of sp.gr. 5·73 with the evolution of considerable heat and when heated suddenly it hisses and gives off vapour while transforming. This vitreous form of arsenic oxidises in the air readily especially at about 50°. The yellow or γ-form of arsenic has a sp.gr. of 2·03 and crystallises in the cubic system ; it is extremely sensitive to all forms of light. It can be preserved for some time by keeping it below −60° in the dark. It is obtained by distilling arsenic in an aluminium tube in a current of carbon dioxide the distillate being suddenly cooled (Erdmann and Unruh, Z. anorg. Chem. 1902, **32**, 437).

The brown or amorphous form has a sp.gr. of 3·67–4·13; these modifications are regarded as due to differences in molecular complexity or as arising from the same quantity of matter distributed throughout a varying space (Kohlschütter, Frank, and Ehlers, Annalen, 1913, **400**, 268 ; Durrant, J.C.S. 1919, **115**, 134).

Krafft and Knocke (Ber. 1909, **42**, 202) found that ordinary arsenic commences to volatilise at 96° in vacuo and that its boiling-point under 760 mm. is 554°. Widely differing figures for the melting-point and boiling-point have been published. Arsenic softens very slowly when kept at 500° in an evacuated sealed tube. Several authors found melting-points between 814° and 818°, including Heike (Z. anorg. Chem. 1921, **118**, 254), 814·5°, and Horiba, 817°–818°, under 35·8 atmospheres (Kon. Acad. Wetensh. 1923, **25**, 387). The unusual relationship between the melting- and boiling-points has been ascribed to rapid volatilisation, simulating ebullition, at a temperature below the true boiling-point. Deep reddish-brown sols of colloidal arsenic have been obtained by an electrolytic method employing an arsenic anode in an alkaline bath. The alkaline sol oxidises rapidly in air, but not if rendered neutral or acid (Lecoq, Compt. rend. 1910, **150**, 700 ; *cf.* Auger, *ibid.* 1907, **145**, 718). Arsenic oxidises in moist air at the ordinary temperature. When heated in air it burns with a bluish flame forming arsenious oxide and giving off a garlic odour. The powder obtained by exposing arsenic to air, a mixture of unaltered arsenic and arsenious oxide, is used in the manufacture of fly papers.

Powdered arsenic thrown into chlorine ignites forming the trichloride; with the aid of heat arsenic combines with bromine, iodine, and sulphur. Boron, silicon, and carbon do not form compounds. Arsenides of certain metals are formed by heating the metal with arsenic. Hydrochloric acid has little action on arsenic, but it is rapidly dissolved by nitric acid, aqua regia, or by a mixture of hydrochloric acid and potassium chlorate. When deflagrated with potassium nitrate it forms potassium arseniate.

Detection.—Arsenic compounds when heated on charcoal, give off the characteristic garlic odour and white fumes of arsenious oxide with a white incrustation on the charcoal some distance from the test. Metallic arsenic, and many arsenical minerals, such as mispickel, when heated in a test tube form a blackish, shining, metallic ring or mirror on the cooler portion of the tube, but if heated in a tube open at both ends or if the section of tube containing the metallic mirror is similarly heated the arsenic is oxidised to arsenious oxide which condenses in a ring of white octahedral crystals, their shape being plainly visible under a lens. The white crystals dissolve in boiling water, and the solution shows the usual tests for arsenious oxide. Antimony in like circumstances produces a white ring which is not crystalline and is not soluble in water. Oxides of arsenic require to be mixed with charcoal before they produce the black mirror. Sulphides require the addition of an alkaline carbonate or potassium cyanide. Arsenious oxide, when heated with about 3 parts of sodium acetate, evolves the offensively smelling "cacodyl," actually cacodyl oxide $[As(CH_3)_2]_2O$.

When hydrogen is generated in a liquid containing an arsenious compound, the arsenic combines with it and passes off as the gaseous hydride; many very delicate tests are based on this reaction.

(1) *Fleitmann's test.*—The solution is mixed with excess of potassium hydrate, a piece of pure zinc, or of magnesium or aluminium foil inserted, and the solution heated. A piece of filter paper moistened with silver nitrate is held over the mouth of the tube. If arsenic is present, hydrogen arsenide is generated and reduces the silver nitrate producing a greyish or purplish colour. Antimony does not give this reaction. Fleitmann's test is therefore a ready means of detecting arsenic in presence of antimony; it is not, however, so delicate as Reinsch's, Marsh's, or the electrolytic method.

(2) *Gutzeit's test.*—The solution to be tested is acidified with hydrochloric acid and treated with zinc preferably in the presence of stannous chloride. The mixture of hydrogen and hydrogen arsenide evolved is first passed over lead acetate paper to remove hydrogen sulphide and then passes up a tube containing discs of paper soaked in mercuric chloride solution, which decomposes the hydrogen arsenide with precipitation of metallic arsenic on the paper; the stains thus obtained are compared with standard stains. Improved forms of apparatus for carrying out this test have been described by Stubbs, White, and Cribb (Analyst, 1927, **52**, 699) and A. J. Linsey (*ibid.* 1930, **55**, 503). Linsey's apparatus is made entirely of glass, the stains formed are of uniform size and tint and the loss of arsenic is reduced to a minimum. A full description of the Gutzeit test suitably modified for different substances and quantitative, is contained in The British Pharmacopœia, 1932, 559–573. Lockemann, in his modification of the test, claims a sensitivity of 10^{-7} g. As (Z. anal. Chem. 1933, **94**, 322).

(3) *Marsh's test.*—This or Reinsch's test is generally used in toxicology. Many precautions must be taken in the destruction of organic matter, the removal of nitrates, etc., and standard books on analytical chemistry or the extensive literature must be consulted for the details of the method. The solution acidified with hydrochloric acid is introduced into an apparatus in which hydrogen is generated by means of pure sulphuric acid and zinc. If the solution contains arsenic, hydrogen arsenide is formed, and with the hydrogen is passed through a drying tube containing calcium chloride and lead acetate-cotton wool, and then through a drawn-out glass tube which is heated at one spot with a burner; the hydrogen arsenide as it passes over the heated portion is decomposed, and a black ring or mirror of arsenic is deposited in the capillary portion of the tube just beyond the flame. Here the capillary is cooled by wrapping round it some cotton lint through which water is siphoned from a beaker. The apparatus should be kept in action for about an hour, and the mirror obtained compared with freshly prepared standards. A blank experiment must always be performed to ascertain the purity of the zinc, the acid and all the reagents and apparatus with which the test material has come in contact. The presence of iron in the zinc or of mercury in the solution is liable to retard or entirely prevent the evolution of hydrogen arsenide. The zinc is sometimes inactive and a preliminary treatment with dilute copper sulphate solution or a 2% cadmium sulphate solution followed by washing the zinc has been recommended (A. C. Chapman, Analyst, 1906, **31**, 3; 1907, **32**, 247; H. E. Cox, "Chemical Analysis of Foods," 1926, 69; Extra Pharmacopœia, 1935, 50). Billiter (Helv. Chim. Acta, 1923, **6**, 773) uses electrolytic zinc which does not require activating, prepared by electrolysing a *N*-solution of zinc sulphate in *N*/10 sulphuric acid, using a pure zinc anode and a silver cathode, with a current of 3–4 amperes at 6 volts. Lockemann (Angew. Chem. 1935, **48**, 199) states that in the region of 10^{-6} g. As the Marsh process is liable to positive errors. His improvements (Z. angew. Chem. 1905, **18**, 416, 491) had raised the sensitivity to 10^{-7} g., Billiter's to 10^{-8} g. (Helv. Chim. Acta, 1918, **1**, 475) and 10^{-9} g. (*ibid.* 1923, **6**, 258, 771). Scheucher (Monatsh. 1921, **42**, 411) by applying Bettendorff's test as a micro-reaction to invisible mirrors detected 10^{-8} g. The glass of Kjeldahl flasks may contain 0·5% As. Concentrated sulphuric acid boiled for 2 hours in one of these flasks extracted 2×10^{-6} g. As, in 4 hours 2×10^{-5} g. Ordinary toxicology is usually concerned with quantities of arsenic larger than 10^{-5} g., but where the sample is small, and in

physiological research a serious error may be introduced, in view of the general use of these flasks in the destruction of organic matter. Lockemann advises the use of quartz vessels, and recommends crystallised calcium chloride, fused to a smooth mass, as a drying agent, since complete dryness is not required, and hydrogen arsenide is liable to decomposition by sharp fragments or fine powders. Reagents should be kept in porcelain bottles, as arsenic has not been detected in porcelain. Colley and Lockwood (J.S.C.I. 1929, **48**, 226T) modified the Conjoint Committee apparatus (1902) by using a drying tube 2½ in. long, tightly packed with cotton-wool allowing room for a small plug of lead acetate wool, and thus avoided the formation of zinc mirrors and obtained uniform coherent arsenic mirrors with standard amounts of arsenic.

"Pickling all glass apparatus by a preliminary boiling with dilute hydrochloric acid before use" is recommended by the Sub-Committee on the determination of arsenic, lead, and other poisonous metals in Food Colouring Matters (Analyst, 1930, **55**, 102). For separating arsenic from very dilute solutions such as sea-water, ferric sulphate and ammonia in slight excess are added and the liquid boiled. The precipitated ferric hydroxide, which contains the arsenic originally present, is dissolved in dilute sulphuric acid and tested by Marsh's method. The arsenic mirror may be distinguished from that produced by antimony by the following tests. (1) It quickly dissolves in a freshly prepared solution of sodium hypochlorite, the antimony mirror under these conditions is very slowly soluble and is insoluble in a stale, hypochlorite solution. (2) The arsenic stain dissolves very slowly in yellow ammonium sulphide, the antimony film dissolves quickly leaving an orange yellow residue on evaporation. (3) If the stain is dissolved in a drop of nitric acid and evaporated, a drop of ammonia placed on the residue and evaporated, addition of a drop of silver nitrate solution causes the formation of brick red silver arsenate. Antimony does not give the colour.

Reinsch's test.—If a piece of clean copper foil is immersed in a solution of an arsenious compound acidified with hydrochloric acid and the solution boiled, the copper becomes coated with a grey film of arsenic. Ferrous sulphate should be added if the solution contains arsenates. A blank test should be made as hydrochloric acid frequently contains arsenic. The copper is removed, washed, dried at a moderate temperature, and heated in a test tube, when a crystalline sublimate of arsenious oxide forms on the colder part of the tube (*v. supra, Detection*). It is not sufficient to observe the octahedral form of the crystals. Wormley (Amer. J. Pharm. 1880, **52**, 195) under certain conditions obtained similar crystals from antimony stains; specific tests for arsenic should be applied. The conditions for Reinsch's test have been studied by Evans (Analyst, 1923, **48**, 357, 428 ; *cf.* Leffmann, *ibid.* 1930, **55**, 684). Evans uses a thin copper wire dipping ¼ inch into the liquid instead of foil. In his modified form (*l.c.* 428) 0·01 mg. **As** in 100 c.c. of the special reagent can be detected, by boiling for one hour. Selenium, bismuth, antimony, and mercury stains are also produced in Reinsch's test. Cowley and Catford (Pharm. J. 1904 [4], **19**, 897) dissolve the stain in bromine water, add potassium hydroxide solution, boil, filter, and test the filtrate with the molybdate reagent.

Feigl's test.—A few drops of a cold saturated solution of ammonium molybdate are added to the test solution, followed by addition of stannous chloride dissolved in hydrochloric acid. On warming, the blue colour disappears completely if no arsenic is present, and the solution becomes yellow to brown. If one part per million of arsenic is present, the blue colour persists. The blue colour due to traces of arsenic may thus be obscured, but is revealed if the solution is shaken with amyl alcohol (Feigl and Neuber, Z. anal. Chem. 1923, **62**, 380). Truog and Meyer have studied the reaction (Ind. Eng. Chem., Analyt. Ed., **1**, 136).

Reppmann's Spot Test.—A drop of a solution of an arsenious compound is placed on filter paper, to this are applied successively one drop each of conc. hydrochloric acid, 0·5% Kairin solution (N-ethyl-8-hydroxytetrahydroquinoline) and 1% ferric chloride solution. The paper is then warmed gently on a microscope slide. A brownish-red spot indicates arsenic. Antimony and bismuth do not give the reaction. Mercury, lead, and copper interfere. The limit quantity of arsenic is 6×10^{-10} g. **As** and the limit of concentration 10^{-7} g./c.c. Arsenic compounds are first reduced with hydrazine sulphate (Z. anal. Chem. 1934, **99**, 180). Under similar conditions Gutzeit (Helv. Chim. Acta, 1929, **12**, 720, 829) obtained a blue-green spot with alcoholic 8-oxyquinoline.

Bettendorff's test.—Arsenious or arsenic compounds dissolved in conc. hydrochloric acid, when mixed with excess of a solution of stannous chloride also in conc. hydrochloric acid, and the mixture boiled, yield a brown precipitate. The reaction is complete when the acid has a sp.gr. of not less than 1·123 ; there is no precipitate with acid of 1·1 sp.gr. Antimony does not give the reaction. Mercury, gold and selenium, if present, are also precipitated, the arsenic is separated from the first by centrifuging, from the two latter by sublimation. As a microchemical reaction : 1–2 cu. mm. of test solution and 4–8 cu. mm. of a solution of 1 part $SnCl_2$ in 2 parts of hydrochloric acid, sp.gr. 1·19, are placed in a capillary tube which is sealed and heated for 5 minutes in a bath of boiling amyl alcohol, and centrifuged. A precipitate visible under the microscope is obtained with 10^{-8} g. **As** in a dilution of 1 : 250,000 (Scheucher, Monatsh. 1921, **42**, 411). Faint arsenic mirrors from Marsh's test are dissolved and transferred to the capillary tube for identification, the test is not so successful in the original tube. If tin foil is substituted for the stannous chloride in Bettendorff's reaction, antimony is precipitated while arsenic compounds are reduced to hydrogen arsenide, detected by mercuric chloride paper (Tananaev and Ponomarjev, Z. anal. Chem. 1935, **101**, 183). In this way 0·01% arsenic in antimony may be detected.

The article CHEMICAL ANALYSIS should be consulted for the electrolytic test for arsenic and for quantitative methods. The following properties of arsenic compounds, utilised in some of the methods, are of general interest. Arsenic trichloride and tribromide are easily volatile in the vapour of the corresponding halogen acid, the distillate under controlled conditions may contain, in addition, selenium and germanium, but only traces of antimony. Arsenic does not volatilise when its solution in aqua regia is evaporated, the residue may contain selenium, etc., but germanium vaporises. Hydroxylamine hydrochloride does not cause a precipitate with the soluble compounds of arsenic, but precipitates selenium. Arsenic oxide is reduced to the arsenious state by distilling with hydrobromic acid ; similarly in sulphuric acid solution it liberates iodine from potassium iodide and is itself reduced to arsenious oxide. In neutral or alkaline solution, arsenious oxide is oxidised by *N*/10 iodine. Arsenic acid, unlike antimonic acid, may be precipitated as silver arsenate from a solution of the mixed acids in an ammoniacal solution of ammonium fluoride. For this purpose the mixed sulphides are taken nearly to dryness with nitric acid and the residue dissolved in dilute hydrofluoric acid, ammonia added, and the liquid boiled with potassium persulphate (M'Cay, J. Amer. Chem. Soc. 1928, **50**, 368).

Spectrography.—Hartley enumerated the following lines in the spark spectrum of a 1% arsenious chloride solution, 2859·7, 2779·5, 2350·1, 2288·9, only 2779·5 was photographed with a 0·1% solution. He described the spectrum as very poor. de Gramont found the sensitive rays were 2860·5, *2780·2*, 2745·0, 2349·8, *2288·1*. The ultimate rays (italicised) are those last to disappear, when the quantity of arsenic is reduced ; a quartz spectrograph was employed (Twyman, Wave Length Tables, London, 1923). Riedl (Z. anorg. Chem. 1932, **209**, 356) identified 2×10^{-8} g. As in the arc spectra of samples of zinc and lead containing 0·02%. The sensitivity was less with solutions unless the arsenic was first separated on the tips of varnished copper electrodes left for 12 hours in 1 c.c. of a slowly evaporating hydrochloric acid solution, $0{\cdot}5\times10^{-6}$ g. could thus be detected. The line relied on was 2349·8. (For references to recent publications *see* K. Heller, Mikrochemie, 1933/34, **14**, 370.)

Alloys of arsenic.—Arsenic alloys with most metals, in many cases in atomic proportions, the compounds thus formed being known as arsenides. Many natural arsenides occur as minerals.

The alloys may be prepared (1) by fusing the metals with arsenic under a layer of borax, or in an atmosphere of inert gas ; (2) by reducing the arsenite or arsenate of the metal with potassium cyanide ; and (3) in some cases—as with gold, silver, and copper—by placing arsenic in a solution of a metallic salt. W. Spring (Ber. 1883, **16**, 324) has obtained crystalline alloys of arsenic with other metals by repeatedly compressing a mixture of the finely divided constituents at 6,500 atmospheres. The arsenides $RuAs_2$, $RhAs_2$, $PdAs_2$, $IrAs_2$, and $PtAs_2$ have been prepared by heating a mixture of the metal chloride with an excess of arsenic in a current of hydrogen.

When heated out of contact with air, arsenical alloys usually lose a portion of their arsenic ; heated in air the arsenic is oxidised, a portion volatilising, and the remainder forming an arsenite or arsenate of the metal. When heated with nitre, arsenates are produced.

The presence of arsenic generally renders an alloy more brittle, more fusible, and brighter. In Pattinson's process it tends to render the lead crystals smaller, and thus lengthens the time required for draining. Its alloys with iron, zinc, and tin are brittle ; with gold and silver, brittle, and grey ; and with lead and antimony, hard, brittle, and fusible. The addition of about 2 parts arsenic to 1000 lead causes the small shot in falling down the tower to form spheres, instead of elongating, as they have otherwise a tendency to do. The arsenic is frequently added in the proper proportions in the form of an alloy of lead and arsenic known as " temper " ; this is prepared by fusing together arsenious oxide and lead. Metallic arsenic or white arsenic with charcoal is added to the charge in copper refining furnaces when the copper is used for the manufacture of fire-box plates, as these have to contain from 0·3 to 0·5% arsenic. In speculum metal the added arsenic sometimes reaches 2%. Britannia metal often contains arsenic as also do certain brasses used in high temperature work. Lead-base alloys for battery grids, bearings, electric cable sheathing and anodes for zinc electrolysis usually contain under 0·5% arsenic.

With potassium and sodium, arsenic forms alloys which evolve arseniuretted hydrogen when placed in water. With platinum it forms a fusible alloy, which was formerly used to facilitate the working of that metal. It forms an amalgam As_2Hg_3 (Dumesnil, Compt. rend. 1911, **152**, 868).

COMPOUNDS OF ARSENIC.

Arsenic trihydride. *Hydrogen arsenide. Arseniuretted hydrogen. Arsine.* AsH_3.—This gas is formed whenever hydrogen is liberated in a solution containing arsenious acid or an arsenite (*cf. supra, Detection*). Hydrogen activated by α-particles from radium unites directly with arsenic producing the trihydride, but ordinary hydrogen has no action (Wendt and Landauer, J. Amer. Chem. Soc. 1920, **42**, 930). It is best prepared either by the action of dilute sulphuric acid on zinc arsenide (Ogier, Ann. Chim. Phys. 1880 [v], **20**, 17) or of water on sodium arsenide (Janowsky, Ber. 1873, **6**, 216) or calcium arsenide (Lebeau, Ann. Chim. Phys. 1902 [vii], **25**, 470). It is a colourless neutral gas with a disagreeable garlic odour, slightly soluble in water and very poisonous; m.p. −113·5°, b.p. −55° (Olszewski, Phil. Mag. 1895 [5], **39**, 188). de Forcrand (Compt. rend. 1915, **160**, 467) prepared the hydrate $AsH_3\cdot6H_2O$ by compressing the gas in presence of water. At 0° its dissociation pressure is 0·806 atmospheres. Hydrogen arsenide decomposes when heated, depositing arsenic perceptibly at 300°, which volatilises at 440°, so that the mirror ceases to be formed above this temperature. It is a powerful reducing agent and according to the concentration and temperature of the solutions of silver, gold, and platinum salts with which it reacts, precipitates either the metal or a metallic arsenide. The reaction with excess of silver nitrate solution giving the metal is used for absorbing and estimating the gas, unless only traces are present, when it is best absorbed by bromine water, and the resulting arsenic acid determined as magnesium pyroarsenate (*v.* CHEMICAL ANALYSIS).

The hydrogen evolved when commercial metals and alloys are treated with acids may contain hydrogen arsenide, *e.g.* in the bronzing of brass with arsenical solutions and in pickling as a preliminary operation to the tinning or galvanising of iron or steel.

There are two solid hydrides of arsenic. The ***dihydride*** AsH is formed as a by-product in the preparation of the trihydride from metallic arsenides and is prepared by adding a hydrochloric acid solution of arsenic trichloride to an ethereal solution of stannous chloride. It is a brown powder, insoluble in water, alkalis, and in most acids, but is oxidised by nitric acid to arsenic oxide (*cf.* Montignie, Bull. Soc. chim. 1935 [v], 2, 1020). *Hydrogen tetra-arsenide* is an insoluble red powder deposited when the trihydride is passed into a solution of stannic chloride in hydrochloric acid :

$$4AsH_3+5SnCl_4=As_4H_2+10HCl+5SnCl_2$$

(Weeks and Druce, Rec. trav. chim. 1925, **44**, 970 ; Moser and Brukl, Monatsh. 1924, **45**, 25).

Arsenious oxide.—*Arsenic trioxide. Arsenious anhydride. White arsenic. Arsenic*, in many official and medical publications. As_2O_3, often written As_4O_6.

Preparation.—Arsenious oxide is obtained as a by product from the roasting of mispickel or other arsenical minerals associated with ores of copper, tin, lead, gold, zinc, tungsten, nickel, cobalt, etc.

From one works alone, the Boliden smelter on the Gulf of Bothnia, Sweden, the arsenious oxide obtained as a by-product is capable of meeting the world's requirements of some 50,000 tons per annum. Here the copper ores treated contain unusually high percentages of arsenic in addition to high gold values and some silver, and the disposal of this arsenic has proved a serious problem. At first the crude arsenic flue dust was mixed with cement or placed in large concrete cylinders and sunk in the deep waters of the Gulf of Bothnia. This proved expensive and a concrete storage structure capable of holding 120,000 tons of crude arsenic has been built.

The roasting operation may be carried out in reverberatory furnaces, rotating or mechanically operated furnaces of various types, and the arsenious oxide contained in the effluent gases collected in long cooling flues, bag-houses, or by Cottrell electrical precipitators. From copper and lead smelting furnaces the flue dust may be re-smelted in reverberatory furnaces producing a matte, the arsenic being again volatilised and condensed. Lead bag-house dust, sometimes carrying 30% arsenious oxide, is often mixed with sulphides and roasted, an enriched arsenical dust being obtained for subsequent treatment, together with a clinker which is returned to the blast furnaces.

The ores may be roasted in a reverberatory furnace. In a common form, the furnace bed is flat, 12–15 ft. long and 7–9 ft. wide in the middle ; the arch is about 2 ft. above the bed, and sinks gradually towards the flue, at which end there is an iron door, through which the ore is raked (Fig. 1).

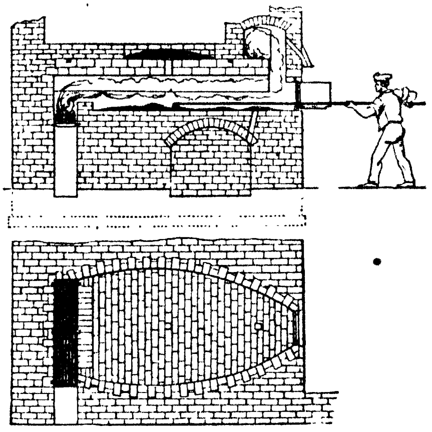


FIG. 1.

A charge of dried ore is introduced through a hopper over the centre of the fire-bridge and spread over the furnace bed. The heat is raised to dull redness and the ore is frequently stirred to ensure thorough oxidation of the arsenic and sulphur. In about 10 hours these have been expelled as oxides, and the arsenious oxide together with some of the sulphur collects in the flues. The spent ore is removed through an aperture in the bed, which is closed with an iron door during calcination.

Two such furnaces are sometimes built side by side, separated by a wall, and with their flues uniting. The furnace beds slope gently towards a narrow fireplace. In the first instance the ore is introduced through a number of doors on each side of the furnace. As the ore is worked downwards its place is constantly supplied by fresh ore through an opening in the roof.

Oxland and Hocking's Calciner has been largely used for roasting arsenical ores (Figs. 2 and 3). It consists of a wrought-iron cylinder, which is 32 ft. in length, and lined with sufficient firebrick to leave 4 ft. clear internal diameter. Four longitudinal ribs of firebrick within the furnace, leave sufficient space at the upper end for the continuous supply of the ore. The cylinder is generally mounted in an inclined position, the slope being usually $\frac{1}{2}$ to 1 in. per ft., and is turned by means of a turbine or water-wheel once in 8 or 10 minutes upon friction-wheels.

The dried, finely powdered ore is introduced through an Archimedean screw, or from a hopper at the upper end, and in the revolution of the tube becomes lifted to a certain height by the ribs of firebrick, and falls in a fine stream through the hot blast. In passing through, the ore is completely oxidised, the arsenic burning off first, and finally reaches the lower end of the tube, where it falls into a chamber beneath. A calciner of the above size will roast 6 to 7 tons of ore in 24 hours. In this furnace the amount of air required is minimised, thus rendering the condensation less difficult. The amount of fuel used is also small.

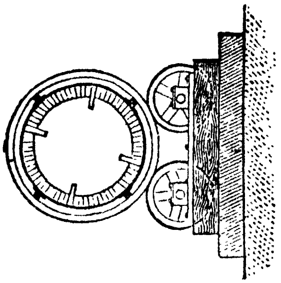


Fig. 3.

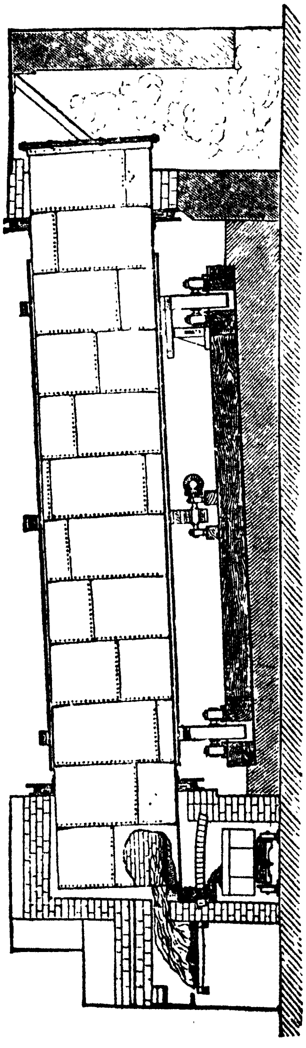


Fig. 2.

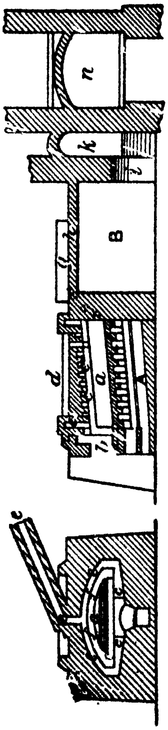
As already pointed out, the sources and methods of recovery of white arsenic have changed very considerably in recent years, practically the whole of the material put on the market being obtained as a by-product from the treatment of ores of various metals for their values other than arsenic, instead of from minerals chosen for their high arsenic content. The first treatment such ores have to undergo is generally a roasting operation and whatever type of furnace is used the arsenic passes off as oxide ; in this way all the modern forms of roasting furnaces must be included as possible producers of arsenic.

In addition to roasting furnaces, smelting furnaces such as blast furnaces produce quantities of flue dust which is collected and, in the case of copper, lead, and tin works, this dust frequently contains arsenic which is recovered.

Condensation of the oxide.—The vapours passing off in the roasting or other operations are carried through chambers so arranged that the gases come in contact with a very large condensing surface before escaping into the air.

These chambers are cleared at intervals, two sets of chambers are frequently used, so that one set may be working while the other is being cleared. After passing through cooling flues the fumes are usually filtered through suitable bags or electrically precipitated by the Cottrell method (*v.* LEAD).

The oxide produced by all processes except those in which muffle furnaces are used, such as shown in Fig. 4, is known as "arsenical soot," and is impure, containing carbon and sulphur



Longitudinal Section.

Transverse Section.

Fig. 4.—MUFFLE FURNACE.

compounds ; when so mixed it is of a dark-grey colour and requires to be resublimed.

The condensing chambers connected with the muffles are in a lofty building called the "poison tower" (Giftthurm), Fig. 5. The gases traverse, by a sinuous course, a series of chambers, depositing the purest product in the lower ones, that in the upper chambers containing sulphur. Being comparatively pure, the product does not usually require refining, but may be at once converted into arsenical glass. The workmen engaged in clearing the chambers are clothed in leathern garments with glazed apertures for the eyes, and wear wet cloths over their mouths and noses to absorb the irritating fumes.

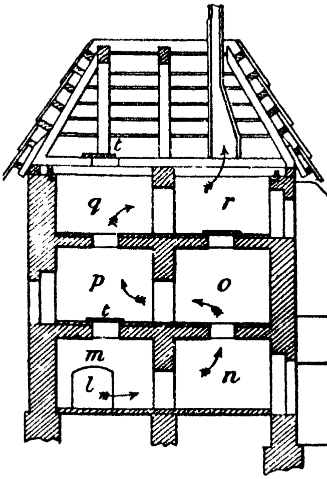


Fig. 5.—Vertical Section of "Poison Tower."

From the point of view of recovery the methods used for the condensation and collection of the arsenical fume are of more importance than the type of furnace used for its formation. In Swedish practice, the arsenic, about 11%, is almost entirely removed from the ore during the preliminary roast and the roaster gases must first be cooled below the condensation point of arsenious oxide (193°). The coolers are large chambers of sheet iron in which about one-third of the oxide is condensed. The remaining two-thirds is deposited in Cottrell electrical precipitators, and it has been found that, in order to secure efficiency of condensation, the gases must be cooled to 150° before entering the precipitators. Screw conveyors are used to remove the oxide from the coolers and precipitators to the storage chamber (A. G. P. Paten, Eng. & Min. J. 1932, **133**, 339).

Refining or Resublimation.—For this purpose a reverberatory furnace is used, which is usually much shorter than that in which the calcination is performed. The arsenical soot is charged from the top and paddled down through doors at the side, more being added as sublimation proceeds. The fuel used is smokeless, usually a mixture of anthracite and coke. The sublimate is collected in chambers similar to those already described. It is white, glistening, and minutely crystalline. It is ground between millstones, and thence fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

Arsenic glass, or *vitreous white arsenic*, is prepared by volatilisation of the powder under slight pressure. For this purpose cast iron pans or pots are used. In the case of the former, each pan is 2 ft. in diameter and surmounted by a bell 2 ft. 6 in. high. The pan is heated to a cherry red, and about ¼ cwt. of refined white arsenic introduced through an opening in the top of the bell, which is then closed with a plug. In about 2 hours the whole has evaporated and condensed on the bell as a transparent glass ; more white arsenic is then introduced and condensed, until after 24 hours the glass has reached a thickness of about 1 in. The later charges, owing to the condensing surface being hotter, require about twice as long to condense as the first.

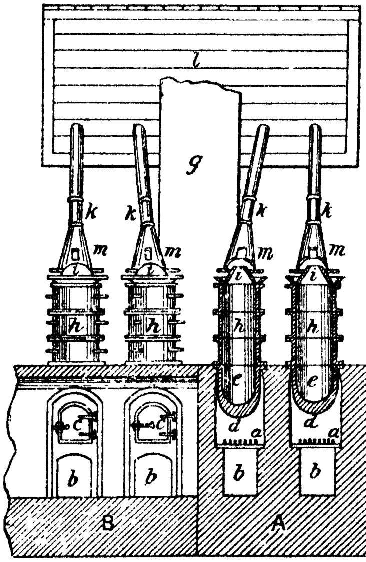


Fig. 6.

The subliming pots are generally deeper and of greater capacity (Fig. 6) ; they are surmounted by iron drums and conical caps, which condense the "glass" and open into condensing chambers. The temperature is carefully regulated. The arsenic glass produced amounts to about 92% of the refined white arsenic used.

Analyses of Arsenic Powder and Arsenic Glass.

(1) Powder from Altenberg, from the condenser of a tin roasting furnace, near the furnace end (Lampadius).

(2) Do. from further end of condenser (Lampadius).

(3) Do. from Oberschlema (Lampadius).
(4) Arsenic glass from Andreasberg (Streng).

	(1)	(2)	(3)	(4)
Arsenious oxide .	90·1	95·85	94·31	98·2
Arsenious sulphide .	2·05	0·32	1·03	—
Bismuth	—	—	0·25	—
Sulphur	0·73	0·71	0·50	—
Ore-dust . . .	5·51	2·05	3·05	—
Antimonious oxide .	—	—	—	1·68

Properties and Uses of Arsenious Oxide.—There are three well-known modifications of this substance and a fourth, or γ variety, has been discovered recently by Smits and Beljaars as a transformation product of the common octahedral, or β form (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34,** 1141, 1318). The ordinary variety is the crystalline sublimate deposited by the vapour of the oxide on surfaces below 250° and from aqueous solutions of the oxide. The white lumps of the commercial article frequently contain portions of the amorphous vitreous form, arsenic glass (*v. supra*). The densities of different samples differ widely, the extremes are 3·529 and 3·874, suggesting the presence of more than one allotropic form. The density of the mineral *arsenolite* is 3·70–3·72. When heated to about 193°, it sublimes without melting. Tamman found the melting-point in a sealed tube to be 313°. Smits and Beljaars (*l.c.* 1318) found the m.p. 272·1 under 26·1 mm. pressure. The boiling-point is 465° (Tamman). Monoclinic, sometimes termed prismatic, or α-arsenious oxide condenses from the vapour of arsenious oxide at temperatures about 250°, and is formed by heating the ordinary β-form with a trace of water in a sealed tube to 218° for several hours. It crystallises from hot saturated solutions of arsenious oxide, in sulphuric acid, 1 : 4, or in alkaline arsenites. Its density is 4·15 (Groth). The mineral *claudetite*, monoclinic As_2O_3, has the density 3·9–4·2. The m.p. is 312·3° at 66·1 mm. Little is known of the γ-variety except the m.p. 289·6° at 40·7 mm., and some physical constants determined by Smits and Beljaars (*l.c.* 1141). Mol. heat of sublimation (g. cal.), α-, 23,676 ; β-, 29,833 ; γ-, 21,130. Mol. heat of fusion (g. cal.), α-, 8,942 ; β-, 15,099 ; γ-, 6,396. Mol. heat of vaporisation (g. cal.), α-, 14,734.

Vitreous or amorphous arsenious oxide is formed by cooling arsenious oxide which has been melted in a sealed tube, or by condensing the vapour on surfaces heated to about 400°. Freshly prepared, it is a transparent glassy mass, but on exposure to air, or on boiling with water, it becomes white and opaque by formation of the octahedral form. The density is variously stated between 3·702 and 3·884. It is more soluble in water than the β-variety, the solutions slowly deposit octahedral crystals, the quantity retained in solution finally corresponds to the solubility of the β-form (Winkler, J. pr. Chem. 1885 [ii], **31,** 247). The vitreous and α- and β-forms of arsenious oxide, when dissolved in hot dilute hydrochloric acid and the solutions allowed to cool, yield octahedral crystals which are momentarily luminescent (Guinchant, Compt. rend. 1905, **140,** 1101, 1170 ; Gernez, *ibid.*, **140,** 1134).

The density and refractive index of aqueous solutions of arsenious oxide have been determined by Anderson and Storey (J. Amer. Chem. Soc. 1923, **45,** 1102). They estimated also the solubility expressed as g. As_2O_3 per 100 g. water : 0°, 1·21 g. ; 15°, 1·66 g. ; 25°, 2·05 g. ; 39·8°, 2·93 g. ; 48·2°, 3·43 g. ; 62°, 4·45 g. ; 75°, 5·62 g. ; 98·5°, 8·18 g. The following values of d^{25}_{25} are recorded for solutions containing the number of grams stated per litre of solution : 1·796 g., 1·0014 ; 3·212 g., 1·0025 ; 5·060 g., 1·0039 ; 6·425 g., 1·0050 ; 7·184 g., 1·0057 ; 8·561 g., 1·0068 ; 10·13 g., 1·0080 ; 11·35 g., 1·0089 ; 12·85 g., 1·0102 ; 14·368 g., 1·0113. The refractive index, measured with an immersion refractometer, varies in a linear manner with the concentration. The number of grams of arsenious oxide per litre is represented by $-10{,}062{\cdot}7+7{,}550r$, where r is the refractive index at 22°. The P_H of the solution by the Sorensen indicator method was 6·6. Wood (J.C.S. 1908, **93,** 1) found the dissociation constant $6{\cdot}3\times10^{-10}$ by the saponification method, $26{\cdot}5\times10^{-10}$ from conductivity methods. Arsenious acid, H_3AsO_3, believed to be present in the solution, is therefore one of the weakest inorganic acids, resembling boric acid. Cryoscopic measurement of the solution gave 99·17 as the molecular weight, a value which indicates that a hydrate of arsenious oxide is present. Vapour density determinations by V. Meyer (Ber. 1879, **12,** 1112) at 1,560°, gave a value corresponding to As_4O_6. At 1,800° the vapour consists almost entirely of As_2O_3 (Biltz, Z. physikal. Chem. 1898, **19,** 385).

Arsenious oxide is not oxidised by exposure to air at ordinary temperatures and very slowly in solution in hydrochloric acid. Oxidising agents, *e.g.* iodine, bromine, nitric acid, hydrogen peroxide, convert it into arsenic acid, an explosion may result from the use of concentrated hydrogen peroxide. Heated with charcoal it is reduced to the metal, nascent hydrogen forms hydrogen arsenide, hydrogen sulphide forms arsenic trisulphide. It does not combine with water to form a hydrate which can be isolated, ortho-, meta-, and pyro-arsenious acids, H_3AsO_3, $HAsO_2$, and $H_4As_2O_5$ have not been obtained although their salts are known. Addition of mannitol or sorbitol increases the acidity of the aqueous solution but not to the same extent as in the case of boric acid (Roth and Schwartz, Ber. 1926, **59** [B], 338). Arsenious oxide can be volatilised from a hydrochloric acid solution containing methyl alcohol by passing a current of air through the liquid maintained at 55° ; 45 c.c. of methyl alcohol suffice for the evaporation of 0·1 g. arsenious oxide which is collected in an absorbing solution (Duparc and Ramadier, Helv. Chim. Acta, 1922, **5,** 552). The reaction between arsenious oxide and sodium or potassium carbonate in boiling aqueous solution proceeds slowly but almost the whole of the theoretical quantity of carbon dioxide is evolved if a current of hydrogen is passed through the solution (Vanzetti, Gazetta, 1925, **55,** 110 ; *cf.* Millar, Pharm. J. 1928, **120,** 214). Concentrated hydrochloric acid dissolves arsenious oxide forming arsenic trichloride in an equilibrium reaction. Hydrobromic and hydriodic acids react similarly, according to the equation :

$$As_2O_3+6HX \rightleftharpoons 2AsX_3+3H_2O$$

Arsenious oxide is highly poisonous, very small doses are prescribed in skin diseases, and as a general tonic, usually in the form of Fowler's Solution, which contains 1% w/v dissolved in potassium hydroxide solution which is then neutralised with hydrochloric acid. It is slowly excreted and there have been many cases of cumulative poisoning. Peasants in Styria have habitually taken considerable quantities of an arsenical earth, which is said to increase their weight and appetite. The lack of toxic action was believed to be due to a tolerance acquired through the long continued use. An explanation may be that the solid drug has not been absorbed. Schwartz (J. Pharm. Exp. Ther. 1922, **20**, 181) found that the toxicity of arsenious oxide varied greatly with its fineness of pulverisation. In other experiments on dogs the tolerance observed was due to impeded absorption. The serious epidemic of arsenic poisoning in Northern England in 1900 has already been mentioned (p. 468). A prolonged study has since been made of the arsenic in food and drugs and in raw materials from which arsenic can pass into the manufactured article. Malt may be contaminated with arsenic from the coal or coke used for heating the kiln (Royal Commission Report on Arsenical Poisoning, 1903).

A suspension of freshly precipitated ferric hydroxide and light magnesia is prescribed as an antidote in cases of acute arsenical poisoning. Lockemann and Lucius (Z. physikal. Chem. 1913, **83**, 735) studied the adsorption of arsenious oxide by ferric hydroxide precipitated in the solution. The total adsorption follows the formula, $E=\beta A^p$, in which E represents the number of mg. of ferric hydroxide, A the number of mg. arsenious oxide per 100 c.c., and β and p are constants which differ for different temperatures ; more ferric hydroxide is required at higher temperatures. The adsorption is rapid and reaches its limiting value in less than one hour (Boutaric and Perreau, J. Pharm. Chim. 1928 [viii], **8**, 211). Ageing of the ferric hydroxide for four months resulted in a 50% decrease in adsorption (Sen, J. Physical Chem. 1927, **31**, 419).

Arsenious oxide is used in the manufacture of insecticides, sheep dips, weed-killers, wood preservatives, antifouling paints for ships, arsenical soap for taxidermy, and in glass-making to remove the green colour produced by ferric oxide; in enamelling; as a constituent of white fire in pyrotechny; for the manufacture of arsenic acid, and of a number of pigments and colour lakes. It has a limited application in calico printing as a reducing agent and in the form of a solution in glycerin (1·5 lb. arsenious oxide : 8·5 lb. glycerin) known as "arsenic standard," in conjunction with alumina paste, the resulting aluminium arsenite being a mordant for basic colours. The use of a solution of arsenious oxide in sulphuric acid has been claimed for the removal of phosphine from acetylene (G.P. 179994).

Of the 15,500 tons of white arsenic produced in the United States in 1930, 70% was used in the manufacture of insecticides, 19% in weed-killers and wood preservatives, 5% in the glass industry, and the remaining 6% for minor purposes (V. C. Heikes, "Mineral Resources of U.S.A.," 1930, pt. I, Bureau of Mines).

In analytical chemistry a 0·1*N* solution of arsenious acid is employed in the analysis of bleaching powder. It is a standard substance in iodimetry and has been proposed as one in alkalimetry (Menzies and McCarthy, J. Amer. Chem. Soc. 1915, **37**, 2021).

Sodium arsenite.—Sodium meta-arsenite, $NaAsO_2$, or $Na_2O{\cdot}As_2O_3$, is prepared from the theoretical quantities of sodium hydroxide and arsenious oxide by prolonged shaking at 25° in presence of water (Stavenhagen, J. pr. Chem. 1895 [ii], **51**, 11). It is manufactured by mixing arsenious oxide with powdered caustic soda and adding a little water when the reaction spreads through the entire mass. The salt is very soluble in water, the solution, when rendered alkaline with alkali hydroxide, precipitates insoluble arsenites from solutions of salts of the heavy metals. Lithium arsenite, but not lithium arsenate, is soluble, and a separation of the two acids may be thus effected (T. Gasper y Arnal, Ann. Chim. Analyt. 1933 [ii], **15**, 193). Gutmann has described the use of sodium arsenite as a reagent for loosely combined reactive oxygen, sulphur, and nitrogen in organic and inorganic compounds (Z. anal. Chem. 1925, **66**, 224). Persulphide sulphur is distinguished from disulphide sulphur, the former oxidises the arsenite in presence of water, the latter does not react. Thiocyanates form Na_3AsSO_3 (Ber. 1923, **56** [B], 2365). Iodoform is converted into methylene iodide showing that only one of its iodine atoms is present in the labile tervalent form (Z. anal. Chem. 1924, **65**, 246). Pasteur's preparations of sodium arsenites (J. Pharm. Chim. 1848 [iii], **13**, 397) are not uniform products (Stavenhagen, *l.c.*). It is doubtful whether sodium ortho-arsenite, Na_3AsO_3, has been prepared, unless Vanzetti's product was this substance (Gazetta, 1925, **55**, 109). Sodium pyroarsenite, $Na_4As_2O_5$, or $2Na_2O,As_2O_3$, was prepared by Stavenhagen (*l.c.*) by the method above described. It crystallises with 9 molecules of water.

Scheele's green was formerly considered to be acid copper ortho-arsenite, $CuHAsO_3$, but according to Bornemann (Z. anorg. Chem. 1922, **124**, 36) it is a normal arsenite,

$$3CuO{\cdot}As_2O_3,xH_2O.$$

The composition was found to vary with the method of preparation ; the greater the excess of alkali employed the richer is the product in copper oxide. It is manufactured by mixing 422 gallons of a 2% solution of copper sulphate with 30 gals. of a solution obtained by dissolving together 35 lb. of soda ash and 11 to 30 lb. of arsenious oxide according to the shade desired. The mixture is stirred, and a dilute solution of caustic soda is added until all the copper is precipitated. The precipitated pigment is washed, filter-pressed, and dried at about 35°.

It can be made in a range of tones from pale to dark green. Formerly largely used for calico printing and for wall-papers, it is now employed to some extent as a wood preservative. It was sprinkled over the streams in the Campania in experiments made to destroy the larvæ of mosquitos, where, owing to the movement of the water, petroleum could not be used. (Private communication.)

Schweinfurt green, *emerald green, Paris green, copper acetoarsenite,*

$$3CuO{\cdot}As_2O_3{\cdot}Cu(C_2H_3O_2)_2$$

—This brilliant green pigment is manufactured by mixing a hot (90°C.) solution of copper sulphate, 206 lb., with a solution obtained by dissolving together 88 lb. of soda ash and 172 lb. of white arsenic, in hot water. The dull olive green precipitate of copper arsenite is allowed to stand for a short time. An excess of cold dilute acetic acid (64 lb. $C_2H_4O_2$) is then added, there is a vigorous evolution of carbon dioxide and in about an hour the conversion of the arsenite into acetoarsenite is completed. The product is washed, filter-pressed, cut into slabs with copper knives and dried at about 35°. The pigment is used as an oil and water colour. Like Scheele's green, it is very poisonous. The effect of mould growth has already been mentioned (p. 469). It has some application as an insecticide and wood preservative. Zinc meta-arsenite is used as a timber preservative. The toxicity of metal arsenites for various insects has been found to be in the order $Mg > Pb = Ca = Cu > Fe > Zn$.

Arsenic oxide. *Arsenic pentoxide. Arsenic anhydride,* As_2O_5.—An opaque, white, amorphous powder, it is produced when arsenious oxide is acted upon by an oxidising agent. On the large scale, jacketed retorts provided with stirring gear are used to contain a mixture of arsenious oxide and nitric acid, sp.gr. 1·35. A current of air conveys the nitrous fumes to a tower packed with coke where they are absorbed in water. Further quantities of arsenious oxide and nitric acid are added when the reaction moderates. The contents of the retorts are withdrawn to enamelled iron evaporators where they are concentrated to 75°Bé. The liquid is sold as arsenic acid. If evaporated to dryness and the residue heated at 180°–200°, it yields arsenic oxide. Air as an oxidant in presence of iodine, is claimed in U.S.P. 1992053. Published values of the density of the oxide vary from 3·7342 (Karsten) to 4·3 (Auger). Landolt Börnstein Tables, 1927, give 4·086. When heated above 400° it decomposes into oxygen and arsenious oxide. When heated with lead or zinc it is reduced to arsenic which then forms a metallic arsenide. Heated with hydrochloric acid it yields arsenic trichloride and chlorine and reacts with hydrogen sulphide forming arsenic pentasulphide. It is hygroscopic and dissolves slowly in water to form a solution containing over 77% As_2O_5 at 16°. The aqueous solutions exhibit the properties of arsenic acid, and have a strongly acid reaction, the dissociation constant k at 25° is 5×10^{-3}. The residue on evaporation is not one of the three acids, ortho-arsenic acid, H_3AsO_4, pyro-, $H_4As_2O_7$, meta-, $HAsO_3$, but the existence of the following hydrates seems to be established, $As_2O_5,4H_2O$ which crystallises in the cold, and $3As_2O_5,5H_2O$ formed above 40° (Auger, Compt. rend. 1933, **197**, 1639; Menzies and Potter, J. Amer. Chem. Soc. 1912, **34**, 1452). Rosenheim and Antelmann (Z. anorg. Chem. 1930, **187**, 385) describe the hydrate $As_2O_5,2H_2O$ or $H_4As_2O_7$, but its existence is disputed by Auger (*l.c.*). The hydrate $2As_2O_5,3H_2O$ was said to be a definite compound (Joly, Compt. rend. 1885, **100**, 1221; **101**, 1262; *cf.* de Passillé, *ibid.* 1935, **200**, 1852). Schiff's determinations of the density of arsenic acid solution calculated to 15°/4° (Landolt Börnstein Tabellen, 1923, I, 411) are as follows, the concentration is expressed as g. H_3AsO_4 in 100 g. solution. H_3AsO_4 7·5 g., d_4^{15} 1·0485; 15·0 g., 1·1041; 22·5 g., 1·1654; 30·0 g., 1·2336; 45·0 g., 1·3956; 67·4 g., 1·7332. Nietzki's table of densities at 16°/4° relate to more concentrated solutions containing the following numbers of grams As_2O_5 per 100 g. solution (Landolt Börnstein, *l.c.*): 56·5 g., 1·758; 60·1 g., 1·847; 65·3 g., 1·994; 70·2 g., 2·153; 75·5 g., 2·360; 77·4 g., 2·442.

Arsenic acid is reduced to arsenious acid by sulphurous acid and to hydrogen arsenide by nascent hydrogen. It acts as an oxidising agent liberating iodine from potassium iodide in acid solutions, and was formerly used in the manufacture of the dyestuff magenta. Its characteristic insoluble salts are magnesium ammonium arsenate, a white crystalline precipitate, and the brick-red silver arsenate. The colour change produced on treating the former salt with silver nitrate is valuable for the identification of traces of arsenic acid. In its behaviour with indicators and with ammonium molybdate it resembles phosphoric acid.

Sodium arsenate, $Na_2HAsO_4,12H_2O$. Disodium hydrogen arsenate is manufactured by heating a mixture of arsenious oxide, caustic soda, and sodium nitrate, extracting the product with a solution of sodium carbonate, and concentrating the extract to crystallisation. Considerable quantities are obtained as a by-product of the Harris process of refining lead. It is used in calico printing as a substitute for cow-dung, it yields insoluble compounds with any uncombined iron or aluminium mordants and thus prevents staining in the dye bath. Trisodium arsenate Na_3AsO_4 is formed with evolution of hydrogen when arsenious oxide or sodium arsenite is heated to redness with a large excess of sodium hydroxide.

Arsenates of various metals have found an increasing application in the control of insect pests; of the arsenical sprays in general use, lead arsenate is stated to be the least harmful to foliage. The toxicity of metal arsenates has been found to be in the following order,

$$Pb > Cu > Ca > Mg > Zn > Fe$$

(Fulmek, Fortschr. Landw. 1929, **4**, 209).

Arsenate of lead finds its chief use as an insecticide in poison sprays and dusts for the destruction of the codling moth, plum curculis, cabbage worm, potato bug, tobacco hornworm, and other pests which injure fruits and vegetables. It is available in three forms, the acid salt, the basic salt, and a colloidal lead arsenate which was placed on the market in 1931 (Chem. Age, 1931, **25**, 381). The salt $2PbO \cdot As_2O_5,H_2O$ can be made by boiling lead mud from sulphuric acid chambers with sodium arsenate (F.P. 766969, 3/4/1933, Soc. Produits Chimiques de la Loire). Arsenates of magnesium and manganese are also used as insecticides. Calcium arsenate is largely used as an insecticide ; it is more effective than lead arsenate in combating the ravages of the boll weevil in cotton-producing countries. It is manufactured from milk of lime and arsenic acid.

Arsenic sulphides.—Arsenic forms three well-known sulphides, As_2S_2, As_2S_3, and As_2S_5, the two former occurring as minerals. Arsenic subsulphide, As_3S, was prepared by Farmer and Firth (J.C.S. 1926, 119) by reducing acid solutions of arsenious or of arsenic oxide with sodium hyposulphite (hydrosulphite). The dark brown precipitate, insoluble in colourless ammonium sulphide, appears to be identical with the substance obtained by Scott (J.C.S. 1900, **77**, 651). Tetra-arsenic trisulphide, As_4S_3, orange yellow crystals, was obtained by heating realgar with sulphur (Szarvasi and Messinger, Ber. 1897, **30**, 1343).

Arsenic disulphide or **Realgar** (*q.v.*), As_2S_2. Prepared by fusing together arsenic and sulphur in the proper proportions, is manufactured by distilling a mixture of arsenical ores, *e.g.* löllingite, with iron pyrites, or with sulphur, in tube furnaces :

$$FeAs_2+3FeS_2=2AsS+4FeS.$$

The crude realgar collects in conical sheet iron receivers and is remelted with sulphur in iron pans, and run into moulds when the required orange-red colour has been obtained. Native realgar, sp.gr. 3·5–3·6, is sometimes ground and sold without sublimation. The furnace product, sp.gr. 2·3–3·3, does not correspond in composition to As_2S_2 (As 70·05%), but contains from 61–64% As and 39–36% S. It is used in tanning as a depilatory for white glove leather, and in pyrotechny as a constituent of blue fire and of "Indian fire," a signal light, which consists of realgar 2, sulphur 7, and saltpetre 24 parts. Lead chromate has replaced it as an artist's pigment; in tanning, sodium sulphide has partly supplanted its use. Arsenic disulphide exists in two modifications, the red α-form d^{19} 3·506, changes at 267° into the black β-form, d 3·254. It is insoluble in water and dilute acids, but is decomposed by heating with alkalis or alkaline sulphides.

Arsenic trisulphide or **Orpiment.** *Yellow sulphide of arsenic. Auripigmentum. King's yellow,* As_2S_3.—This sulphide is formed as a yellow precipitate when hydrogen sulphide is passed through a solution of arsenious oxide in hydrochloric acid. Commercial orpiment, made by heating arsenious oxide with 3–4% sulphur, is a lemon to orange-yellow sublimate containing 2·7–3·4% As_2S_3, and has d 3·46. It was formerly much used as a pigment under the name of King's yellow, but is not permanent on exposure to light and is replaced by chrome yellow. It is used as a depilatory in tanning, as an insecticide, and in pyrotechny for blue lights.

The sol of arsenic trisulphide has played an important part in colloid chemistry, it is made by passing hydrogen sulphide through a solution of arsenious oxide (Schulze, J. pr. Chem. 1882 [ii], **25**, 431). Arsenic trisulphide is soluble in caustic alkali solution, from which it is precipitated by addition of hydrochloric but not of acetic acid, in the latter case the salts $KAsO_2$ and $KAsS_2$ remain in solution. Wünschendorff (Bull. Soc. chim. 1929 [iv], **45**, 889) has prepared a number of sodium (5), potassium (3), and ammonium (2) thioarsenites.

Arsenic pentasulphide, As_2S_5, is a lemon-yellow powder, paler than arsenic trisulphide, precipitated by hydrogen sulphide from solutions of arsenic pentoxide in hydrochloric acid (Usher and Travers, J.C.S. 1905, **87**, 1370). It has no industrial importance. It unites with the sulphides of the alkali metals forming thioarsenates, M_3AsS_4, their solutions precipitate the salts of the heavy metals; with ammonia and the alkali hydroxides, it yields a series of salts, sulphoxyarsenates, M_3AsSO_3, $M_3AsS_2O_2$, M_3AsS_3O.

Arsenic chloride. *Butter of arsenic. Caustic oil of arsenic.*—Glauber prepared this substance in 1648 by distilling a mixture of arsenious oxide, sulphuric acid, and sodium chloride, it is also obtained by distilling arsenious oxide with concentrated hydrochloric acid and by the action of chlorine on arsenic. It is a colourless oily liquid fuming in air, b.p. 130·2°/760 mm., m.p. $-18°$ and d^{20} 2·1668. With a small quantity of water it yields the compound $AsCl(OH)_2$, but with an excess, arsenious oxide and hydrochloric acid are formed. It is readily volatilised when boiled with hydrochloric acid, but a 0·1*N* solution, 1*N* as regards acidity, may be concentrated to half its bulk without loss of more than one-thousandth part of the arsenic present. Arsenic pentachloride does not exist at ordinary temperatures, although its formation has been claimed (and disputed) by saturating arsenic trichloride with chlorine at $-33°$.

Arsenic tri-iodide, AsI_3, orange-red hexagonal crystals, is prepared by heating a mixture of iodine and arsenic and crystallising the product from toluene or carbon disulphide. It has m.p. 141°, b.p. about 400°, d 4·39. It is used in medicine for purposes similar to those of arsenious oxide. C. O. B. and J. N. G.

ARSENIC GLASS *v.* ARSENIC, ARSENIOUS OXIDE.

ARSENIC MOULD, "Gosio-gas," *v.* ARSENICALS, ORGANIC, *volatile arsenicals from moulds.*

ARSENICALS, ORGANIC. The organic chemistry of arsenic has received closer attention than that of any other element. Almost from the time of the discovery by L. C. Cadet de Gassicourt in 1760 of his "fuming arsenical liquid," organic compounds of arsenic have aroused the curiosity of chemists, an interest which has deepened in recent years as a result of the impetus received from chemotherapy and chemical warfare.

Cadet's "fuming liquid," obtained by the distillation of equal parts of arsenious oxide and potassium acetate, had an intolerable odour and the property of spontaneous inflammability in air. In spite of investigations by Guyton de Morveau, Morel and Durande, and later by Thénard, it was left to the classical researches of Wilhelm Bunsen (Pogg. Ann. 1837, **40**, 219; **42**, 145) and to the fruitful suggestions of Berzelius to prove that the liquid contained the oxide of an arseniuretted radical, a group containing arsenic, carbon, and hydrogen which remained of constant composition when the oxygen was replaced by halogens, sulphur, or cyanogen. This radical was given the name Kakodyl (Gr. *Kakos-odyl*) by Berzelius, so that the main constituent of Cadet's liquid is cacodyl oxide, which was prepared in a pure state by Bunsen by hydrolysing cacodyl chloride with potassium hydroxide. He also oxidised the oxide to cacodylic acid and finally isolated the radical cacodyl itself, which, indeed, is a constituent of the "fuming liquid." The inner structure of this radical was not investigated by Bunsen, but Frankland, Kolbe, and others have shown that it may be regarded as tervalent arsenic associated with two methyl groups. It is, therefore, $AsMe_2$, and in its free state this univalent complex doubles on itself to give cacodyl, As_2Me_4. The chloride and the oxide then have the structures:

$$Me_2As{-}Cl \qquad Me_2As{-}O{-}AsMe_2$$

In more recent times greater attention has been devoted to the aromatic rather than to the aliphatic arsenicals, although an interesting study of the action of cyanogen bromide on alkyl- and arylalkyl-arsines has been made by Steinkopf and his co-workers, while war-time investigations produced a noteworthy series of compounds in the β-chlorovinylarsines (Lewisite).

Arsenical compounds containing aromatic radicals were first investigated by Béchamp (Compt. rend. 1860, **50**, 872; **51**, 356; 1863, **55**, 1172), who, studying the oxidising action of arsenic acid on aniline, noted that a colourless condensation product could be obtained which functioned as a monobasic acid. Béchamp assumed it to be an anilide of orthoarsenic acid, $C_6H_5{\cdot}NH{\cdot}AsO(OH)_2$, but Ehrlich and Bertheim (Ber. 1907, **40**, 3292) proved that it was *p*-amino-phenylarsonic acid,

$$NH_2{\cdot}C_6H_5{\cdot}AsO(OH)_2,$$

the sodium salt of which is the *Atoxyl* of therapeutics.

The curative value of atoxyl in trypanosomiasis led Ehrlich to institute extensive researches for the discovery of other arsenicals which should be useful in this and related diseases. His discovery that certain of the tervalent arsenobenzenes had a pronounced action in protozoal diseases resulted in the production of *Salvarsan* or "606" in 1910, while *Neosalvarsan* or "914" was discovered in 1911. Since then countless other arsenobenzenes have been prepared in the search for even more efficient drugs for the arsenical treatment of syphilis. The success of these arsenobenzenes temporarily diverted attention from the quinquevalent arsonic acids, but the discovery of the diazo synthesis of such acids (Bart, G.P. 250260; B.P. 568, 1911) and, later, the preparation of tryparsamide by Jacobs and Heidelberger in 1919, led to an active resumption of the study of these quinquevalent compounds. Fourneau and his co-workers at the Pasteur Institute in Paris have studied *Stovarsol* and many similar derivatives and consequently a somewhat clearer idea of the relationship between chemical constitution and therapeutic action has been obtained; this knowledge has also been enhanced by the researches of H. King and his collaborators and of the chemists of many manufacturing firms.

The past few years have seen a tendency to revert to tervalent arsenicals both of the arsenobenzene series and also of the simpler $R{\cdot}As{\cdot}O$ type. In the former case many complex substances have been made containing also antimony and bismuth, while interest in the latter has been stimulated by the discovery that they may be obtained in soluble form as thioarsenites. These sulphur derivatives are of interest because of their connection with ideas regarding the trypanocidal action of arsenicals. The arsonic acids are inert *in vitro* but become active *in vivo* and it has been assumed that this activity is caused by the reduction of the impotent quinquevalent acids to the effective tervalent arsenoxides by the thiol (glutathione) present in the body tissue. Furthermore, Voegtlin, Dyer, and Leonard have suggested that the arsenoxides so formed exert their action by combining with the glutathione present in the trypanosomes.

Several of the arsenic analogues of heterocyclic nitrogen compounds have been made, and of these the phenarsazine derivatives have been the subject of much intensive research, especially on the part of C. S. Gibson in this country and of Razuvaiev in Russia.

CACODYL AND ITS DERIVATIVES (Bunsen, Annalen, 1842, **42**, 14).—*Cacodyl*, $(AsMe_2)_2$, (*tetramethyldiarsine*), a colourless, highly refractive liquid with intolerable odour; b.p. 170°; solidifies at −6°, forming square plates; vapour density 7·1; sparingly soluble in water, is prepared by treating cacodyl chloride with metallic zinc in an atmosphere of carbon dioxide. It inflames spontaneously in air, giving carbon dioxide, water, and arsenious oxide. It behaves as a univalent or tervalent radical, $—AsMe_2$, combining with sulphur and the halogens.

Ethylcacodyl (*tetraethyldiarsine*) is an oil, b.p. 185°–190°, produced, together with *triethylarsine*, $AsEt_3$, b.p. 140°, by the interaction of ethyl iodide and sodium arsenide; it yields, on oxidation, diethylarsinic acid, a soluble crystalline product (Landolt, Annalen, 1854, **89**, 316; **92**, 365).

Dimethyldiisoamylcacodyl, $Me_2As{\cdot}As(C_5H_{11})_2$, is an unsymmetrical diarsine obtained by the following general method (Dehn, Amer. Chem. J. 1908, **40**, 123):

$$R_2AsH + ClAsR'_2 = HCl + R_2As{\cdot}AsR'_2$$

from a secondary arsine and a secondary chloroarsine.

Cacodyl oxide, $(AsMe_2)_2O$, the main constituent of Cadet's liquid, is a heavy oil; b.p.

120° ; d^{15} 1·462 ; solidifies at −25° ; vapour density 7·55 ; sparingly soluble in water. It is prepared by distilling cacodyl chloride with aqueous potassium hydroxide, drying, and redistilling in atmosphere of carbon dioxide (Bayer, Annalen, 1858, **107**, 282).

Cacodyl chloride, colourless liquid, heavier than water; b.p. 100° ; vapour density 4·56 ; is insoluble in water. It has a penetrating, stupefying odour and a marked irritating action on the mucous membrane of the nose.

It is obtained when concentrated hydrochloric acid and mercuric chloride are added successively to Cadet's liquid, and the resulting crystalline magma is liquefied by the addition of more hydrochloric acid and distilled. The distillate containing cacodyl chloride is purified by treatment with calcium carbonate to remove acid, and with calcium chloride to remove water.

Cacodyl cyanide, colourless prisms ; m.p. 33° ; b.p. 140° ; sublimes readily at ordinary temperatures to a vapour which was originally thought to be very poisonous. It is soluble in alcohol and ether, sparingly so in water, and is prepared by interaction between cacodyl and mercuric cyanide :

$$(AsMe_2)_2+Hg(CN)_2=Hg+2AsMe_2CN$$

Cacodyl sulphide, $(AsMe_2)_2S$, colourless oil ; b.p. >100° ; insoluble in water ; miscible with ether and alcohol.

Cacodyl disulphide, $(AsMe_2)_2S_2$, white rhombic plates ; m.p. 50°.

Cacodyl cuprisulphide, $(AsMe_2)_2S,3Cu_2S$, lustrous octahedra.

Cacodylic acid (*dimethylarsinic acid*),

$$AsMe_2O{\cdot}OH$$

(Bunsen, Annalen, 1843, **46**, 2), inodorous, colourless prisms ; m.p. 200° ; is prepared by the oxidation of cacodyl oxide with mercuric oxide under water. It is very stable, especially to oxidising agents ; very soluble in water and alcohol ; it forms crystallisable salts, certain of which have been used in medicine, including sodium cacodylate, $AsMe_2O_2Na,3H_2O$ (Ph. Helv.).

Cacodyl trichloride, Me_2AsCl_3 (Bayer, *l.c.*), which crystallises from ether in prisms or leaflets, is very unstable, fumes in air, and decomposes at 40°–50° into *methyldichloroarsine*, $MeAsCl_2$, and methyl chloride.

Cacodyl carbide, $Me_2AsC{\equiv}CAsMe_2$. This interesting compound is obtained when magnesium acetylene bromide reacts with cacodyl chloride ; the mixture, when worked up in the usual way, yields a colourless oil, b.p. 84·5°/14 mm. It is highly reactive, explodes with nitric acid, and is decomposed by alkalis. The carbide is also moderately poisonous (Wieland, Annalen, 1923, **431**, 30).

Syntheses of Aliphatic Arsenicals.

I. Interaction of an Alkyl Halide with Arsenic or an Alloy of Arsenic (Cahours, Compt. rend. 1859, **49**, 87 ; Annalen, 1862, **122**, 200).—Methyl iodide reacts at 160°–200° with arsenic or with zinc or cadmium alloys of arsenic yielding double salts of the formulæ: $AsMe_4I,AsI_3$; $2AsMe_4I,Zn(Cd)I_2$. From these salts the tetramethylarsonium iodide is obtained on treatment with caustic alkali. If amorphous arsenic is used then the reaction may be carried out at ordinary temperature (Martindale, Congress of Applied Chem. 1909).

II. Interaction of a Metallic Alkyl with an Arsenic Halide.—Zinc dimethyl or methyl magnesium iodide reacts with arsenious chloride or iodide to give trimethylarsine (Hofmann, Annalen, 1857, **103**, 357 ; Jahresber. 1855, 538 ; Hibbert, Ber. 1906, **39**, 160). Replacing the arsenious halide by an alkyl chloroarsine ($RAsCl_2$ or R_2AsCl) enables mixed arsines to be obtained.

The Grignard reagent also reacts with arsenious oxide to produce trialkylarsines, though in the aromatic series secondary arsenoxides, $(R_2As)_2O$, may be formed (Gryszkiewicz-Trochimovski, Rocz. Chem. 1928, **8**, 250 ; Blicke and Smith, J. Amer. Chem. Soc. 1929, **51**, 1558, 3479).

III. Alkylation of Arsenical Oxy-Compounds.—In this process, due originally to G. Meyer (Ber. 1883, **16**, 1440 ; *see also* Klinger and Kreutz, Annalen, 1888, **249**, 147 ; Dehn and McGrath, Amer. Chem. J. 1905, **33**, 138 ; J. Amer. Chem. Soc. 1906, **28**, 351), sodium arsenite is treated at ordinary temperature with alkyl iodide in aqueous-alcoholic solution, giving the sodium alkylarsonate.

More recently, Quick and Adams have standardised the method. The alkyl iodide is replaced by the bromide or chloride, thus obviating any reduction of the arsonic acid by liberated hydrogen iodide, while the reaction is allowed to take place at an elevated temperature and with water alone as the medium (J. Amer. Chem. Soc. 1922, **44**, 805).

IV. Dealkylation of Aliphatic or Mixed Arsenicals.—Quinquevalent tertiary or secondary chloroarsines may, on distillation, lose alkyl halide and so form the corresponding secondary or primary chloroarsines respectively. Thus cacodyl trichloride eliminates methyl chloride at 40°–50° with the production of methyldichloroarsine, $MeAsCl_2$ (Bayer, Annalen, 1858, **107**, 282).

If trialkylarsine cyanobromides are heated *in vacuo* then secondary cyanoarsines are obtained (Steinkopf and Müller, Ber. 1921, **54**, 841).

It has also been suggested that primary chloroarsines may conveniently be prepared by acting with hydrogen chloride on 10-alkyl-dihydrophenarsazines. The latter are easily formed by the Grignard reaction on 10-chlorodihydrophenarsazines (Gibson and Johnson, J.C.S. 1931, 2521 ; Govaert, Compt. rend. 1935, **200**, 1603).

Aliphatic Arsenicals.

Trimethylarsine, $AsMe_3$, colourless liquid, b.p. 52°/736 mm., d^{22} 1·123 ; synthesised by method II above or by distilling tetramethylarsonium iodide with dry potassium hydroxide (Renshaw and Holm, J. Amer. Chem. Soc. 1920, **42**, 1468). The arsine is acted upon by atmospheric oxygen, giving *trimethylarsine oxide* and cacodylic acid ; it also combines directly with halogens, sulphur, and selenium. With methyl iodide it forms *tetramethylarsonium iodide* as a solid crystallising in colourless leaflets which decompose at 170°–180°, and this on treatment with silver hydroxide yields the *tetramethylarsonium hydroxide*, which is a strongly caustic crystalline substance.

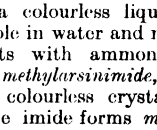
Dimethylarsine, Me_2AsH, colourless liquid with odour of cacodyl, b.p. 35·6° ; spontaneously inflammable in air above 10° (Palmer, Ber. 1894, **27**, 1378 ; Dehn and Wilcox, Amer. Chem. J. 1906, **35**, 3). It is prepared by dropping strong hydrochloric acid on to a mixture of crude cacodyl oxide, amalgamated zinc dust, and alcohol. The dimethylarsine which is evolved is passed through washing and drying agents and is liquefied in a receiver surrounded by a freezing mixture.

Methylarsine, $MeAsH_2$ (Palmer and Dehn, Ber. 1901, **34**, 3594). Volatile, colourless, highly refractive liquid, b.p. 2° ; very poisonous and fumes in air though it is not spontaneously inflammable ; almost insoluble in water but miscible with alcohol, ether, or carbon disulphide ; is prepared by reducing methylarsonic acid with amalgamated zinc dust and alcoholic hydrochloric acid.

Methyldichloroarsine.—Obtained by method IV above as a colourless liquid, b.p. 133° ; somewhat soluble in water and not decomposed thereby. Reacts with ammonia in benzene solution to form *methylarsinimide*, $(MeAs{=}NH)_6$ as tetrahedral colourless crystals, m.p. 205°. With water the imide forms *methylarsenoxide*, while hydrogen chloride regenerates the dichloroarsine (Ipatiev, Razuvaiev, and Stromski, Ber. 1929, **62**, 598).

Methylarsonic acid, $MeAsO(OH)_2$ (Quick and Adams, *l.c.*).—Anhydrous, colourless crystals, m.p. 161° ; soluble in water and alcohol ; decomposes carbonates and forms an ammonium salt. The sodium salt (*Arrhenal* or *New cacodyl*), $MeAsO(ONa)_2,H_2O$, has been used in medicine, as also have sodium dimethylarsinate, $Me_2AsO_2Na,3H_2O$, and the corresponding salts of magnesium, iron, strychnine, guiacol and antipyrine.

Arsenomethane.—Reduction of sodium methylarsonate with hypophosphorous acid yields a yellow oil, b.p. 178°/15 mm., to which the formula $(MeAs)_4$ was assigned, but which has now been shown to be cyclo*pentamethylpentaarsine.*



Exhaustive methylation with methyl iodide leads to tetramethylarsonium mono- and tri-iodides together with methyldiiodoarsine. Distilled under ordinary pressure it yields cacodyl and arsenic. A solid red modification is also known (Palmer and Scott, J. Amer. Chem. Soc. 1928, **50**, 536 ; Steinkopf, Schmidt, and Smie, Ber. 1926, **59**, 1463).

cyclo-*Penta*-n-*propylpenta-arsine* has also been made and gives arsenic and n-*propylcacodyl* on distillation ; the latter is a colourless, mobile liquid, b.p. 168°–170°/15 mm. (Steinkopf and Dudek, Ber. 1928, **61**, 1906).

Triethylarsine cyanobromide, $Et_3As(CN)Br$, colourless, crystalline product, m.p. 67°. Formed by combining triethylarsine with cyanogen bromide in light petroleum ; very susceptible to moisture and easily hydrolysed to *triethylarsine hydroxybromide*, $Et_3As(OH)Br$. The cyanobromide when heated *in vacuo* loses ethyl bromide with production of *diethylcyanoarsine*, m.p. about 50° (Steinkopf and Müller, *l.c.*).

Steinkopf and his co-workers have studied many such cyanobromides, not only of trialkylarsines but also of arylalkyl and triarylarsines. They all behave similarly towards moisture and lose alkyl bromide on heating ; where there are dissimilar groups the one of lowest molecular weight is eliminated. Triphenylarsine cyanobromide does not, however, evolve bromobenzene in this way but undergoes a more complex decomposition (Steinkopf and Schwen, Ber. 1921, **54**, 2791 ; Steinkopf, Donat, and Jaeger, Ber. 1922, **55**, 2597).

β-Hydroxyethylarsonic acid,

$$CH_2(OH)CH_2{\cdot}AsO_3H_2$$

obtained from ethylene chlorohydrin by method III above as a viscous syrup which, on prolonged drying, gives crystals of the acid with one mol. of water. Drying in a vacuum oven produces the anhydrous acid which is extremely hygroscopic ; m.p. 157°–159°. Reduced with sulphur dioxide it forms the *arsenoxide* as a thick viscous liquid which with hydrochloric acid yields the *dichloride* as an oil soluble in water and chloroform.

β-Chloroethyldichloroarsine,

$$CH_2Cl{\cdot}CH_2{\cdot}AsCl_2,$$

colourless oil, b.p. 92°–93°/32 mm., formed when either the above dichloride or arsenoxide is treated with phosphorus pentachloride, phosphoryl chloride, or thionyl chloride ; insoluble in water, readily soluble in organic media ; hot alkali decomposes it with evolution of ethylene, while oxidation under hydrolytic conditions gives β-chloroethylarsonic acid as plates or needles, m.p. 133° (Gough and King, J.C.S. 1928, 2432 ; Edee, J. Amer. Chem. Soc. 1928, **50**, 1394 ; Nekrassov and Nekrassov, Ber. 1928, **61**, 1816 ; Scherlin and Epstein, *ibid.* 1821 ; Soare, Bul. Chim. Soc. Române, 1933, **36**, 75).

β-Chloroethylarsonic acid has been made the starting point of a number of β-*amino* derivatives formed by acting on it with ammonia and amines. Care must be taken that excess of alkali is not used, as this decomposes the acid with production of ethylene.

β-Chloropropylarsonic acid yields similar products, though this acid is stable towards excess of alkali (Gough and King, *l.c.*).

Other halogenoalkylarsonic acids have been made by Backer and Bolt, who have also obtained a number of aliphatic diarsonic acids of the type $AsO_3H_2[CH_2]_nAsO_3H_2$ (Rec. trav. chim. 1935, **54**, 47, 68).

Arsonoacetic acid, $H_2O_3As{\cdot}CH_2{\cdot}CO_2H$. This typical member of the carboxyarsonic acids is made by a modification of method III, in which chloroacetic acid is allowed to act at ordinary temperature on sodium arsenite in the presence of excess of alkali :

$$Na_3AsO_3 + ClCH_2\cdot CO_2Na = NaO_2C\cdot CH_2\cdot AsO_3Na_2 + NaCl$$

The sodium salt is a white powder, easily soluble in water and giving a solution which is alkaline to litmus. The free acid is obtained through the barium or lead salts and forms colourless plates, m.p. 152°, readily soluble in water and alcohol, insoluble in petroleum, benzene, acetone or chloroform.

Reduction of the sodium salt with sodium hypophosphite gives *arsenoacetic acid*,

$$HO_2C\cdot CH_2\cdot As{=}As\cdot CH_2\cdot CO_2H\ ;$$

slender yellow needles, insoluble in water but soluble in bases.

A *tetraarseno*-acid has also been obtained :

$$HO_2C\cdot CH_2\cdot As{=}As-As{=}As\cdot CH_2\cdot CO_2H$$

(Palmer, J. Amer. Chem. Soc. 1923, **45**, 3023 ; Backer and Mulder, Rec. trav. chim. 1936, **55**, 357, 594).

β-Chlorovinyl derivatives of arsenic.—Acetylene reacts with anhydrous arsenious chloride in the presence of aluminium chloride to form a mixture of three unsaturated arsenicals, namely, β-chlorovinyldichloroarsine, ββ'-dichlorodivinylchloroarsine, and ββ'β''-trichlorotrivinylarsine, which are separable by fractional distillation under reduced pressure. These compounds were discovered in America in 1918 during the search for substances useful in chemical warfare and have since attracted considerable attention owing to the powerful toxic and irritant properties of the primary and secondary arsines, a crude mixture of which is known as *lewisite*. *β-Chlorovinyldichloroarsine*, $ClHC:CHAsCl_2$, colourless or faintly yellow liquid, b.p. 76°–77°/12·5 mm., soluble in the usual solvents. Even its dilute solutions have marked vesicant properties. By virtue of its unsaturated nature it readily absorbs halogens ; with dilute alkali it evolves acetylene, though careful treatment with cold dilute ammonia gives the *arsenoxide*, a white crystalline powder, m.p. 143°. Oxidation of the chloroarsine with nitric acid or of the arsenoxide with hydrogen peroxide produces *β-chlorovinylarsonic acid*, $ClHC:CH\cdot AsO_3H_2$, flat hexagonal crystals or fine needles, m.p. 130°, easily soluble in water or alcohol.

ββ'-Dichlorodivinylchloroarsine,

$$(ClHC:CH)_2AsCl,$$

b.p. 108°–109°/10·5 mm., closely resembles the primary derivative but appears to be a somewhat more powerful nasal irritant. The corresponding *arsenoxide* results from the action of sodium ethoxide on an alcoholic solution of the chloroarsine, m.p. 62°–63° ; oxidation with nitric acid in the cold gives the *arsinic acid*, $(ClHC:CH)_2AsO_2H$, m.p. 114°–115°.

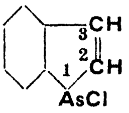
ββ'β''-Trichlorotrivinylarsine,

$$(ClHC:CH)_3As$$

The fraction of the crude mixture boiling between 139°–140°/13 mm. crystallises on cooling, giving long white needles of the tertiary arsine, m.p. 23° ; it is devoid of irritant properties. Careful treatment with bromine in petroleum at low temperature yields the *dibromide* as needles, m.p. 107° ; prolonged heating with methyl iodide at 80° is necessary to form the *methiodide*, m.p. 209° (Lewis and Perkins, Ind. Eng. Chem. 1923, **15**, 290 ; Lewis and Steigler, J. Amer. Chem. Soc. 1925, **47**, 2546 ; Green and Price, J.C.S. 1921, **119**, 448 ; Mann and Pope, *ibid.* 1922, 1754). By using substituted acetylenes, derivatives of the vinylarsines may be made. With arylvinylarsines, however, the reaction sometimes proceeds further and arsindoles are formed. Thus phenyldichloroarsine with acetylene and aluminium chloride yields *β-chlorovinylphenylchloroarsine*,

$$PhClAsCH:CHCl,$$

and this on further treatment with aluminium chloride gives 1-*chloroarsindole*. This compound has also been obtained from o-*vinylphenyldichloroarsine*, $C_6H_5CH:CHAsCl_2$ (Das Gupta, J. Ind. Chem. Soc. 1935, **12**, 627 ; 1936, **13**, 305 ; Mannich, Arch. Pharm. 1935, **273**, 275).



VOLATILE ARSENICALS FROM MOULDS.

Wallpapers and carpets containing arsenical pigments have long been known to be a source of danger owing to the evolution of volatile organic compounds of arsenic of a decidedly toxic character. These gases are produced by the action of certain moulds, especially *Penicillium brevicaule*, on the pigment. Several observers have examined this phenomenon. P. Biginelli in 1900 concluded that the gas was diethylarsine and he obtained well-defined solid derivatives with acidified mercuric chloride, while Klason (Ber. 1914, **47**, 2634) stated that it was diethylarsine oxide. Neither of these substances was known until 1924 when Wigren, who synthesised them, stated that their behaviour towards mercuric chloride was different from that of the gas produced by moulds. More recently, Challenger and his co-workers have conducted a careful investigation on the action of these moulds on arsenical compounds. Four different strains of *Penicillium brevicaule* (*Scopulariopsis brevicaule*), when cultivated on sterile breadcrumbs in the presence of dilute aqueous arsenious acid, each gave trimethylarsine, which was identified by the formation of trimethylarsine dimercurichloride, $Me_3As,2HgCl_2$, trimethylarsine hydroxynitrate, $Me_3As(OH)NO_3$, and benzyltrimethylarsonium picrate,

$$Me_3As(CH_2\cdot C_6H_5)\cdot O\cdot C_6H_2(NO_2)_3$$

The same gas was evolved when sodium methylarsonate or sodium cacodylate was used, though with potassium ethylarsonate the volatile product was dimethylethylarsine. Other alkylarsonic acids give the corresponding dimethylalkylarsines, while diethylarsinic acid forms methyldiethylarsine (Challenger, Higginbottom, and Ellis, J.C.S. 1933, 95 ; Challenger and Ellis, *ibid.* 1935, 396 ; Challenger and Higginbottom, Biochem. J. 1935, **29**, 1757 ; Challenger and Rawlings, J.C.S. 1936, 264).

MIXED ARYL-ALKYL ARSENICALS.

Much of the work in this section is of comparatively recent date and has been actuated largely by the search for compounds capable of optical resolution. They are generally prepared through the Grignard reaction.

Phenyldimethylarsine, $PhAsMe_2$. Obtained originally by the action of zinc dimethyl on phenyldichloroarsine, is usually made by the interaction of bromobenzene, magnesium, and dimethyliodoarsine, or of methyl magnesium iodide and phenyldichloroarsine. Colourless, limpid liquid with repulsive odour, b.p. 85° at 14 mm. ; insoluble in water but miscible with alcohol or benzene. It forms readily double compounds with many inorganic halides and is oxidised in moist air to *phenylmethylarsinic acid*, $PhMeAsO{\cdot}OH$ (Michaelis and Link, Annalen, 1881, **207**, 205 ; Winmill, J.C.S. 1912, 722 ; Burrows and Turner, *ibid.* 1920, 1378 ; 1921, 1448 ; Burrows and Parker, J. Amer. Chem. Soc. 1933, **55**, 4133 ; Burrows, J. Proc. Roy. Soc. New South Wales, 1934, **68**, 72).

Diphenylmethylarsine, Ph_2AsMe, is prepared by methods analogous to those for the previous compound ; colourless, oily liquid with a pungent, fruity odour, b.p. 306°. While not so reactive as phenyldimethylarsine it forms additive compounds with the silver halides (Burrows and Turner, *l.c.* ; Burrows and Parker, *l.c.*).

RESOLUTION OF ASYMMETRIC ARSENICALS.

The optical resolution of arsenicals of the type $[abc]As{:}O$ (or S) and $[abcd]AsX$ has not been so easy as in the case of nitrogen and phosphorus asymmetric compounds. In 1921 Burrows and Turner obtained a solution of *phenyl-β-naphthyl-benzylmethylarsonium iodide* which had a feeble dextro-rotation, while more definite results were obtained by Mills and Raper (J.C.S. 1925, 2479), who resolved into its optical isomers the compound dl-p-*carboxyphenylmethylethylarsine sulphide*,

$$(HO_2C{\cdot}C_6H_4)MeEtAs{:}S$$

prepared as follows: p-*tolylmethylethylarsine*, obtained from p-*tolylmethyliodoarsine* by the Grignard reaction, is oxidised with neutral potassium permanganate to p-*carboxyphenylmethylethylarsenoxide*, and this is converted into the *sulphide* by saturating its aqueous solution with hydrogen sulphide. It crystallises from water as lustrous needles, m.p. 183°.

1-p-*Carboxyphenylmethylethylarsine sulphide* was prepared by fractionally crystallising the *brucine* salt from water. The final fraction was decomposed by alkali, the brucine removed, and the l-acid precipitated with hydrochloric acid, m.p. 175°–177° ; $[\alpha]^{20°}_{5780} = -19{\cdot}1°$.

The corresponding d-*acid* resulted from the fractionation of the *morphine salt* of the *dl*-acid from alcohol and ether. The acid obtained from this salt melts at 175°–176° and has $[\alpha]^{20°}_{5780} = +18{\cdot}7°$.

p-*Tolylbenzylethylpropylarsonium iodide* with silver d-α-bromo-camphor-π-sulphonate yields a crystalline salt separable into three fractions, one of which yields with potassium iodide the optically active arsonium iodide which, however, racemised rapidly ; $[\alpha]^{5}_{D} = +9{\cdot}11°$ (Kamai, Ber. 1933, **66**, 1779 ; J. Gen. Chem. Russ. 1934, **4**, 184).

Lesslie and Turner have also resolved 10-*methyl-*, 10-*ethyl*, and 10-*phenyl-phenoxarsine*-2-*carboxylic acid*, although the dissymmetry in these cases is preferably ascribed to a folded structure (J.C.S. 1934, 1170 ; 1935, 1051, 1268 ; 1936, 730).

SYNTHESES OF AROMATIC ARSENICALS.

For many years the preparation of aromatic compounds of arsenic was limited to two methods both worked out by Michaelis and his pupils (Ber. 1876, **9**, 1566 ; Annalen, 1880, **201**, 184). To these were added later the Grignard reaction and the diazo synthesis.

I. Interaction of the Arsenic Halide with a Diaryl Derivative of Mercury.—The action of the mercury diaryl, which is produced by the interaction of sodium amalgam and the aryl bromide, proceeds in two stages. In the first the arylarsenic dihalide is formed, *e.g.*,

$$HgPh_2 + 2AsCl_3 = HgCl_2 + 2PhAsCl_2$$

If the reaction is allowed to proceed further there is obtained the diarylarsenic halide :

$$HgPh_2 + 2PhAsCl_2 = HgCl_2 + 2Ph_2AsCl$$

A modification of this method has been employed (Ber. 1914, **47**, 2748), whereby an arylmercuric chloride is heated at 100° with arsenious chloride with the formation of the aryldichloroarsine.

II. Interaction of Sodium with Chloroaryls and Arsenious Chloride (or the corresponding Bromo-derivative).—This process is a modified Fittig's synthesis, *e.g.*,

$$AsCl_3 + 3PhCl + 6Na = 6NaCl + AsPh_3$$

From the tertiary arsine may be formed the dihalides which on heating give the secondary arsine halides :

$$Ph_3AsCl_2 = PhCl + Ph_2AsCl$$

Primary derivatives can be formed by heating the tertiary arsine with arsenious chloride under pressure at 250° ; the secondary compound is also formed at the same time :

$$Ph_3As + 2AsCl_3 = 3PhAsCl_2$$
$$2Ph_3As + AsCl_3 = 3Ph_2AsCl$$

III. Grignard Reaction.—This widely used reaction generally leads to the formation of triarylarsines, though, as indicated above (p. 481), secondary arsenoxides may be obtained by using arsenious oxide in place of the chloride.

IV. Diazo Synthesis.—This important method, first discovered by Bart, is now that most extensively used for preparing the therapeutically important arylarsonic acids. These acids result from the treatment of diazonium salts or alkali diazo-oxides with aqueous sodium arsenite with or without the addition of copper powder or copper salts as catalysts (G.P. 250264, 254345). Mouneyrat (B.P. 142947) has shown that the reaction can be carried out under acid, neutral or alkaline conditions, while Schmidt (Annalen, 1920, **421**, 159) has indicated that the most favourable conditions are obtained in accordance with the equation :

$$PhN_2Cl + AsO_3HK_2 = PhAsO_3HK + KCl + N_2$$

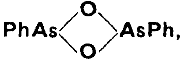
Reduction of some of the arsonic acid takes place if the solution is more strongly alkaline, while poorer yields result under acid conditions, though such conditions are favourable when the benzene nucleus contains strongly acidic substituents.

AROMATIC ARSENICALS.

Phenyldichloroarsine, $PhAsCl_2$ (La Coste and Michaelis, Ber. 1878, **11**, 1883), colourless, highly refractive, viscous liquid, b.p. 252°–254°, possesses a pungent odour and has an irritant action on the skin. It combines with chlorine forming *phenylarsinic chloride*, $PhAsCl_4$ (Michaelis, Ber. 1877, **10**, 622), flattened yellow needles, m.p. 45°, which decomposes violently in water ; dissociates on warming into the dichloride and chlorine, while at 150° it decomposes completely into chlorobenzene and arsenious chloride.

Phenylarsonic acid, $PhAsO(OH)_2$ (Michaelis, *l.c.* ; La Coste and Michaelis, Annalen, 1880, **201**, 184 ; Schmidt, *ibid.* 1920, **421**, 159 ; Bart, *ibid.* 1922, **429**, 75, 110), colourless prisms passing into the anhydride at 158°, soluble in absolute alcohol ; very stable towards oxidising agents ; reducing agents produce either phenylarsenoxide, phenylarsine, or arsenobenzene.

Phenylarsenoxide, $PhAsO$. Obtained either by hydrolysis of phenyldichloroarsine or by reducing the arsonic acid in dilute sulphuric acid with sulphur dioxide. During this latter preparation, the *dimeride*,



$$PhAs\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle AsPh,$$

also is said to be formed. The arsenoxide crystallises from alcohol in colourless crusts, m.p. 119°–120° ; it is soluble in hot alcohol or cold benzene (Michaelis, Ber. 1877, **10**, 263; Steinkopf, Schmidt, and Penz, J. pr. Chem. 1934 [ii], **141**, 301).

Phenylarsine, $PhAsH_2$, colourless liquid, b.p. 148°, soluble in alcohol or ether ; very susceptible to oxidising agents. It reacts with iodine to give either phenyliodoarsine, arsenobenzene, or diphenyldiiododiarsine $(PhIAs-)_2$ (Palmer and Dehn, Ber. 1901, **34**, 3598 ; Blicke and Powers, J. Amer. Chem. Soc. 1933, **55**, 1161 ; 1935, **57**, 749).

Arsenobenzene, $PhAs:AsPh$ (Michaelis and Schulte, Ber. 1881, **14**, 912 ; 1882, **15**, 1952 ; Palmer and Scott, J. Amer. Chem. Soc. 1928, **50**, 536). Obtained by the reduction of phenylarsenoxide with phosphorous acid or, more readily, from phenylarsonic acid and hypophosphorous acid ; light yellow needles, m.p. 196° ; insoluble in water or ether, sparingly soluble in alcohol, soluble in benzene, chloroform, or carbon disulphide.

Diphenylchloroarsine, Ph_2AsCl (La Coste and Michaelis, *l.c.*), well-defined colourless tabular crystals, m.p. 38°–41° ; slight odour, more pronounced on warming. Is more irritant to the skin than the primary chloroarsine. Alkalis hydrolyse it to *diphenylarsenoxide*, crystalline aggregates, m.p. 91°–92°, and this product reduced with phosphorous acid furnishes *phenyl cacodyl* (*tetraphenyldiarsine*), $Ph_2As{\cdot}AsPh_2$, crystalline mass, m.p. 135°. In general, these tetra-aryldiarsines are more conveniently made by acting on diaryliodoarsines with mercury. They are easily oxidised and their solutions absorb instantaneously enough oxygen to form the *peroxide*, $(Ar_2As{\cdot}O-)_2$ (Blicke and others, J. Amer. Chem. Soc. 1929 and onwards).

Diphenylcyanoarsine, $Ph_2As{\cdot}CN$. Employed in large quantities during the later stages of the Great War as an irritant, was manufactured by digesting diphenylchloroarsine with a warm concentrated solution of sodium or potassium cyanide. Colourless crystals, m.p. variously given between 28° and 35°. Hydrolysed by methods used in obtaining carboxylic acids from nitriles it yields *diphenylarsine carboxylic acid*, $Ph_2As{\cdot}CO_2H$ (Sturniols and Bellinzoni, Gazzetta, 1919, **49** [II], 326 ; Morgan and Vining, J.C.S. 1920, 782 ; Steinkopf and Schwen, Ber. 1921, **54**, 2791).

Diphenylarsinic acid, $Ph_2AsO{\cdot}OH$, colourless needles, m.p. 174°. Sparingly soluble in cold water, ether or benzene, more soluble in hot water or alcohol.

Triphenylarsine, Ph_3As (La Coste and Michaelis, *l.c.*), colourless plates from alcohol, m.p. 58°–60°, b.p. above 360° (without decomposition in carbon dioxide). Very soluble in ether or benzene, sparingly soluble in alcohol.

Triphenylmethylarsonium iodide, Ph_3MeAsI, pale yellow leaflets from alcohol, m.p. 176°. Soluble in alcohol or ether, sparingly soluble in water. The *hydroxide* forms prismatic crystals, m.p. 125°–126° ; its aqueous solution absorbs carbon dioxide from the air.

Tetraphenylarsonium bromide, Ph_4AsBr (Blicke and Monroe, J. Amer. Chem. Soc. 1935, **57**, 720). Phenyl magnesium bromide in dry ether is allowed to react with triphenylarsenoxide in hot dry benzene and the residue, after decanting off the solvent, is treated with hydrobromic acid. Colourless glistening needles, m.p. 273°–275° ; it forms a *tribromide* with bromine in acetic acid.

Tribenzylarsine, $(PhCH_2)_3As$ (Michaelis and Paetow, Annalen, 1886, **233**, 60 ; Paetow, Inaug. Dissert. Rostock, 1885 ; Challenger and Peters, J.C.S. 1929, 2610 ; Dodonov and Medox, Ber. 1935, **68**, 1254), colourless monoclinic prisms from alcohol, m.p. 104°. Insoluble in water, sparingly soluble in alcohol ; soluble in ether, benzene and acetic acid. Hot dilute nitric acid oxidises it to arsenic and benzoic acids. Obtained, together with its dichloride and dibenzylarsine trichloride, by the action of sodium on arsenious chloride and benzyl chloride; also together with dibenzylarsinic acid and tribenzylarsenoxide by treating arsenious chloride with magnesium benzyl chloride.

Dibenzylarsinic acid, $(PhCH_2)_2AsO{\cdot}OH$, colourless plates, m.p. 210°, decomposing at higher temperatures ; sparingly soluble in ether, acetone or benzene ; bitter salt taste and irritating to the mucous membrane.

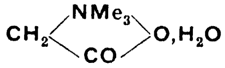
Benzylarsonic acid, $PhCH_2{\cdot}AsO_3H_2$ (Dehn and McGrath, J. Amer. Chem. Soc. 1906, **28**, 354), colourless needles, m.p. 167°.

Benzylarsine, $PhCH_2{\cdot}AsH_2$ (Dehn, Amer. Chem. J. 1908, **40**, 113), light yellow liquid, b.p. 140°/260 mm. ; forms a *platinichloride*, $C_7H_7{\cdot}AsH_2{\cdot}PtCl_4$.

p-*Carboxyphenylarsonic acid* (p-*benzarsonic acid*), $CO_2H{\cdot}C_6H_4{\cdot}AsO_3H_2$ (Michaelis, Annalen, 1902, **320**, 303 ; Ber. 1915, **48**, 870 ; Sieburg, Arch. Pharm. 1916, **254**, 224 ; Lewis and Cheetham, J. Amer. Chem. Soc. 1921, **43**, 2117 ; Bart, *l.c.*). This typical example of the carboxylated derivatives can be obtained by oxidising *p*-tolylarsonic acid either with alkaline permanganate or with nitric acid in a sealed tube at 170°. It is also obtained when *p*-arsanilic acid is diazotised in the presence of cuprous cyanide and the resulting *p*-cyanophenylarsonic acid hydrolysed with potassium hydroxide. The usual method of preparation is by the " Bart " or diazo synthesis on *p*-aminobenzoic acid. The acid forms colourless plates, sparingly soluble in water and hot alcohol.

BETAINES OF AROMATIC ARSENICALS (Michaelis, Annalen, 1902, **320**, 297 ; 1902, **321**, 174).

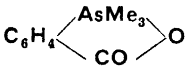
Ordinary betaine, which occurs in the vegetable kingdom and especially in the sap of sugar-beet, has the constitutional formula :



$$CH_2\genfrac{}{}{0pt}{}{\diagup NMe_3 \diagdown}{\diagdown CO \diagup}O,H_2O$$

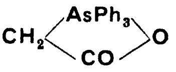
and is allied to trimethylglycine. Analogues containing quinquevalent arsenic, although unknown in nature, have been prepared artificially.

Trimethylarsenibenzobetaine (I) : The hydrochloride of this compound is obtained by oxidising *p*-tolyltrimethylarsonium chloride with alkaline permanganate. The free betaine is obtained by treating the hydrochloride with sodium carbonate and crystallises from dilute alcohol in thin plates.



$$C_6H_4\genfrac{}{}{0pt}{}{\diagup AsMe_3 \diagdown}{\diagdown CO \diagup}O$$

(I)



$$CH_2\genfrac{}{}{0pt}{}{\diagup AsPh_3 \diagdown}{\diagdown CO \diagup}O$$

(II)

Triphenylarsenibetaine (II).—The betaine of the second type is produced by treating triphenylarsine successively with chloroacetic acid and alcoholic potash.

Arsenibetaines have also been obtained by acting on 10-alkyl-5 : 10-dihydrophenarsazines with chloroacetic acid or its ethyl ester and hydrolysing the resulting product with dilute alkali (Razuvaiev, Malinovskii, and Arkina, J. Gen. Chem. Russ. 1935, **5**, 575).

THE USE OF ORGANIC COMPOUNDS OF ARSENIC IN THERAPEUTICS.

Diseases of protozoal origin, such as " sleeping sickness," syphilis, etc., are not generally amenable to serum treatment, while the use of antiseptics, which are inimicable to the existence of the protozoal parasites, is often limited by their injurious action on the tissues of the more highly organised " host." Nevertheless, such parasites are more sensitive to chemical treatment than are the more highly resistant bacteria, so that it is possible to treat these diseases with drugs which react specifically with the protozoa and are comparatively innocuous to the host, as, for instance, in the treatment of malaria with quinine.

The organic compounds of arsenic have been intensively investigated in connection with parasitical infections and a number of successful drugs has been discovered. The success of these substances is due largely to their relatively low toxicity to the higher organism, especially when compared with inorganic derivatives of arsenic, to their ability to interact with the protoplasm of the parasite, to their penetrative power, and to their intensive action so that, although a large fraction of the drug is fairly rapidly excreted unchanged, the residue is still sufficient to provide a parasiticidal concentration.

p-*Aminophenylarsonic acid* (p-*Arsanilic acid*), $NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2$. This substance was first obtained by Béchamp by heating a mixture of aniline and arsenic acid at 190°–200° with stirring. Excess of aniline was removed by steam distillation after the addition of alkali, the crude acid precipitated with hydrochloric acid and purified by crystallisation of the sodium salt from aqueous alcohol. A by-product, *sodium* 4 : 4′-*diamino-diphenyl-arsinate*, remains dissolved in the alcohol. The acid also contains a small quantity of o-*arsanilic acid*, which may be removed by crystallising the mixture from water, in which the *p*-isomer is the less soluble. p-Arsanilic acid forms a *mono-* and *dihydrochloride*, the former being described as an arsonium chloride, $[NH_2{\cdot}C_6H_4{\cdot}As(OH)_3]Cl$, while the second molecule of hydrogen chloride attaches itself to the amine (O. and K. Adler, Ber. 1908, **41**, 932 ; Benda and Kahn, *ibid.* 1674, 2370 ; Pyman and Reynolds, J.C.S. 1908, **93**, 1184 ; Pozdnyakov, J. Chem. Ind. Moscow, 1928, **5**, 530 ; J. Prat, Compt. rend. 1933, **197**, 67).

This condensation is applicable to the homologues of aniline if they contain a free para-position with respect to the amino group. If this position is occupied then the yields of the ortho-substituted arsonic acids are small excepting in the case of *p*-nitraniline (G.P. 219210, 243693 ; B.P. 855 (1908) ; 29196 (1911); 14937 (1908) ; Benda, Ber. 1909, **42**, 3261 ; 1911, **44**, 3294).

The Béchamp condensation also takes place with phenols having a free para-position, *p*-hydroxyarylarsonic acids being formed.

Atoxyl, Sodium p-*arsanilate* (Syn. *Arsamin, Soamin, Natrium Arsanilicum*).—This salt, a white powder containing 2–6 mols. of water of crystallisation, is easily soluble in water to a neutral solution.

Atoxyl was the first arsenical to receive extensive trial in the treatment of protozoal diseases and was widely used by Koch in the cure of trypanosomiasis. Unfortunately, in many cases it produces optic atrophy, so that many attempts have been made to modify it in order to render it less injurious. For this purpose many substituents have been introduced either into the nucleus or into the amino group. Azo derivatives have also been made from the diazotised amine.

Both the ortho- and meta-isomers of atoxyl are inferior to it in trypanocidal effect while, in addition, the former is also more toxic.

DERIVATIVES OF *p*-AMINOPHENYLARSONIC ACID.

Acetyl-p-*arsanilic acid* (Na salt = *Arsacetin, Acetyl atoxyl*).

White plates soluble in dilute sodium carbonate ; the sodium salt crystallises with 3–5 molecules of water.

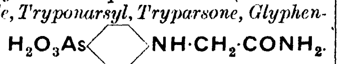
The introduction of an acetyl group into the free amino group of a trypanocidal drug often lowers its toxicity to the host as was found to be the case with arsacetin. This result has naturally led to the study of other *N*-substituted derivatives of atoxyl.

p-*Carbaminophenylarsonic acid*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$$

(*Carbasone*), prepared either by the action of potassium cyanide or cyanogen bromide on *p*-arsanilic acid crystallises from hot water in glistening needles, soluble in caustic alkalis or alkali carbonates and insoluble in dilute mineral acids. It has been extensively used in the treatment of amœbic dysentery (G.P. 213155 ; B.P. 17139 (1908) ; F.P. 392857, 401586 ; Stickings, J.C.S. 1928, 3131).

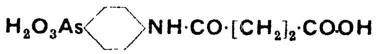
N-*Phenylglycineamide*-p-*arsonic acid* (Na salt = *Tryparsamide, Tryponarsyl, Tryparsone, Glyphenarsine*),



First made in 1919 by Jacobs and Heidelberger (J. Amer. Chem. Soc. 1919, 41, 1587), is still the most widely used arsenical in the treatment of trypanosomiasis. It is obtained by refluxing atoxyl with a large excess of chloroacetamide, the product solidifying out on cooling is treated with hydrochloric acid to remove the unchanged arsanilic acid, and the amide finally purified by dissolving in 25% sodium hydroxide and reprecipitating with acetic acid. It crystallises from hot water in long thin plates ; sparingly soluble in organic solvents and cold water. The *sodium salt* is, however, very soluble in water.

Substitution in the terminal amino group or condensation of atoxyl with *N*-substituted amides of chloroacetic acid has led to the production of many derivatives, though none seems to be as efficient as the parent substance. Homologues have been made from *β*-bromopropionamide, etc., while the ortho- and meta-isomerides are also known (Jacobs and Heidelberger, *l.c.*, *idem ibid.* 1809 ; B.P. 279379 ; Fourneau and Nicolitch, Bull. Soc. chim. 1928 [iv], 43, 1232 ; Gibson, Johnson, and Levin, J.C.S. 1929, 479, 2759 ; Cohen, King, and Strangeways, *ibid.* 1932, 2505 ; Hamilton and Simpson, J. Amer. Chem. Soc. 1929, 51, 3158 ; Raiziss and Clemence, *ibid.* 1930, 52, 2019).

p-*Arsonosuccinanilic acid*,

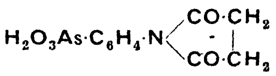


This acid is obtained when atoxyl and succinic anhydride are heated together at 180°, the cooled mass extracted with dilute alkali, and the filtrate acidified with hydrochloric acid. The arsonosuccinanilic acid separates on cooling as silky prisms ; it is insoluble in absolute alcohol. If this acid is heated with atoxyl in the foregoing manner there is formed *succinanilide*-p : p′-*diarsonic acid*,

$$H_2O_3As{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$$

This ill-defined substance, which is insoluble in water and organic solvents, is also made by heating atoxyl with succinic acid.

Succinanil-p-*arsonic acid*,



Hexagonal plates from water, prepared by heating *p*-arsonosuccinanilic acid at 240° ; regenerates the original substance with alkali.

p-*Arsonosuccinanilamides*,

$$H_2O_3As{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO{\cdot}NRR'$$

These amides, produced by the action of amines on the above anil, are colourless solids soluble in hot water and, with the exception of the *piperidide*, are insoluble in alcohol.

Analogous *malonyl*, *glutaryl*, *adipyl*, and similar derivatives of atoxyl have also been made, including the radicals of the dibasic acids up to sebacic acid, so that in the following general formula *n* has values ranging from one to eight.

Certain of the amides having the general formula

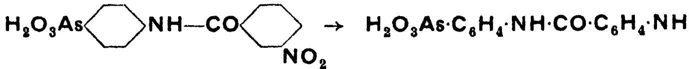
$$NaHO_3As{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}NRR',$$

where R and R′ are either hydrogen or an alkyl group, have been found to possess considerable potency in the treatment of trypanosomiasis and also of syphilis in its various phases. One of these, the sodium salt of *p*-arsonosuccinanilomethylamide,

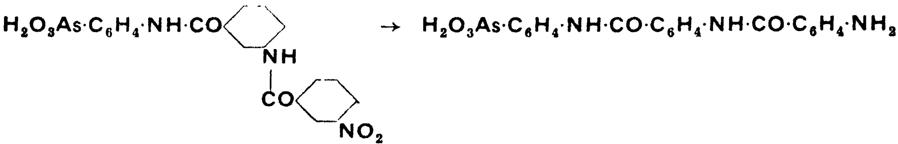
$$NaHO_3As{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO{\cdot}NHMe,$$

has been used with much success in clinical cases. As a drug it goes by the name of S 107 or *neocryl* (Morgan and Walton, J.C.S. 1931, 615, 1743 ; 1932, 276 ; 1933, 91, 1044 ; 1935, 290 ; 1936, 902).

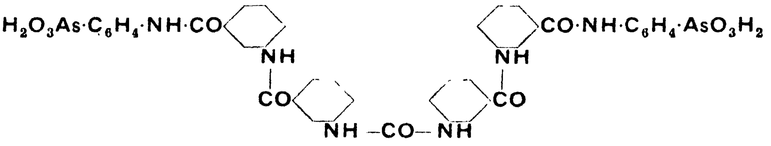
The success of Bayer 205, a purely organic substance, as a trypanocidal drug has led to some attempts to produce a similarly constructed compound but which should also contain the atoxyl structure. Such a product has been obtained from *p*-arsanilic acid by successive nitrobenzoylation and reduction and the final formation of a symmetrical carbamide as in the following scheme :



I. II.



III. IV.



V.

m′-*Nitrobenzoyl*-p-*aminophenylarsonic acid* (I) is obtained by the action of *m*-nitrobenzoyl chloride on *p*-arsanilic acid and crystallises from glacial acetic acid in long needles. Reduction with ferrous hydroxide below 0° gives the amino derivative (II) which forms minute matted needles and is readily soluble in dilute acids.

Repetition of the above processes leads to m″-*nitrobenzoyl*-m′-*aminobenzoyl*-p-*aminophenylarsonic acid* (III) and the corresponding *amine* (IV).

The symmetrical *carbamide* (V) is obtained when an aqueous solution of the sodium salt of (IV) is shaken with phosgene in toluene and the solution made faintly acid to Congo red. The carbamide appears as a gelatinous product having marked colloidal properties. It has no trypanocidal action (King and Murch, J.C.S. 1924, **123**, 2601 ; Hamilton and Major, J. Amer. Chem. Soc. 1925, **47**, 1128).

Derivatives of Diaminophenylarsonic Acids.

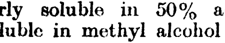
Since the introduction of an amino group into the para-position in phenylarsonic acid decreases its toxicity and increases its trypanocidal activity, it became of interest to study the effect of introducing additional amino radicals. The presence of a second amino group decreases still further the toxicity, but, unfortunately, the activity towards parasites is also decreased while it has disappeared altogether on the introduction of a third amino radical. This decreasing activity is partially connected with the increasing ease with which these substances are eliminated from the body.

3 : 4-*Diaminophenylarsonic acid*,

$$(NH_2)_2C_6H_3{\cdot}AsO_3H_2$$

(Bertheim, Ber. 1911, **44**, 3093 ; Baxter and Fargher, J.C.S. 1919, **115**, 1372 ; Lewis, Cramer, and Bly, J. Amer. Chem. Soc. 1924, **46**, 2058 ; Phillips, J.C.S. 1928, 3124), produced either by the reduction of 3-nitro-4-amino-phenylarsonic acid with alkaline ferrous hydroxide or by the Bart reaction on 4-amino-1 : 2-diacetaminobenzene, crystallises from water in fine needles which retain some of the solvent ; m.p. (with decomposition) 320° ; soluble in alcohols and acetic acid. It is about twenty times less toxic than atoxyl, but has an irregular therapeutic activity owing to its easy elimination from the body. Its low toxicity has led to the study of numerous derivatives in the search for a substance which shall be less readily excreted. A selection of these derivatives is given below.

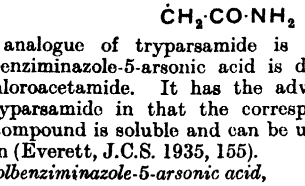
Benziminazole-5 (6)-*arsonic acid* (1 : 3-*Benzodiazole-5-arsonic acid*),



derived from 3 : 4-diaminophenylarsonic acid by refluxing with glacial formic acid crystallises from hot water in minute prisms decomposing about 297°. Sparingly soluble in alcohol ; easily soluble in dilute mineral acids.

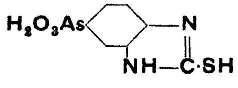
The corresponding *arsenobenziminazole* is obtained in the usual way as a bright yellow powder, fairly soluble in 50% acetic acid, sparingly soluble in methyl alcohol containing hydrochloric acid, but insoluble in other media. It forms a *dihydrochloride* (Baxter and Fargher, J.C.S. 1919, **115**, 1372).

1 (*or* 3)-*Carbamylmethylbenziminazole*-5-*arsonic acid*,



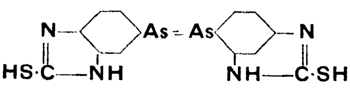
This analogue of tryparsamide is formed when benziminazole-5-arsonic acid is digested with chloroacetamide. It has the advantage over tryparsamide in that the corresponding *arseno* compound is soluble and can be used for injection (Everett, J.C.S. 1935, 155).

2-*Thiolbenziminazole*-5-*arsonic acid*,

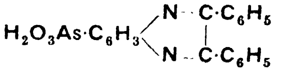


Prepared by the action of thiocarbonyl chloride on 3 : 4-diaminophenylarsonic acid or by oxidation of the corresponding disulphide with $N/10$ iodine ; small buff needles, soluble in hot water or alcohol, insoluble in cold water and dilute mineral acids.

2-*Thiolbenziminazole*-5-*arsonic disulphide* is formed when carbon disulphide reacts with 3 : 4-diaminophenylarsonic acid. When it, or the above arsonic acid, is reduced with sodium hyposulphite there results 5 : 5′-*arseno*-(2-*thiolbenziminazole*) as a light yellow amorphous powder soluble in dilute alkali (Everett, J.C.S. 1929, 670 ; 1930, 2402 ; 1931, 3032 ; G.P. 613349, 563349),



2 : 3-*Diphenylquinoxaline*-6-*arsonic acid,*



$H_2O_3As{\cdot}C_6H_3<\!\!\begin{array}{l}N{-}C{\cdot}C_6H_5\\N{-}C{\cdot}C_6H_5\end{array}$

3 : 4-diaminophenylarsonic acid is refluxed with benzil in alcoholic solution and, on concentration and addition of water, the quinoxaline is obtained as a white or slightly yellow substance insoluble in water, alcohol, or ether ; slightly soluble in acetic acid. When heated with acetic acid and excess hydrobromic acid the dibromoarsine separates in shining plates, m.p. 232° (Lewis, Cramer, and Bly, J. Amer. Chem. Soc. 1924, **46**, 2058 ; 1930, **52**, 229).

Hydroxyaminophenylarsonic Acids.

The hydroxyl group causes an even greater increase in parasiticidal power than the amino group and, moreover, the position is not of paramount importance. The hydroxyarsonic acids alone have not been much used in therapy, but the hydroxy-amino series contains several notable drugs. Of these the more important are the 3-amino-4-hydroxy- and 4-amino-2-hydroxyphenylarsonic acids. These drugs often manifest both trypanocidal and spirillocidal properties.

3-*Amino*-4-*hydroxyphenylarsonic acid* (*Fourneau* 189) (Fargher, J.C.S. 1919, **115**, 990 ; Ehrlich and Bertheim, Ber. 1912, **45**, 756 ; Jacobs, Heidelberger, and Rolf, J. Amer. Chem. Soc. 1918, **40**, 1580 ; B.P. 3087 (1915) ; G.P. 224953). Produced by the reduction of the 3-nitro derivative which, in turn, may be obtained by the Bart reaction on 2-nitro-4-aminophenol or by nitration and subsequent hydrolysis of either 4-dimethylamino- or 4-chlorophenylarsonic acid. The product is purified by recrystallising from hot water in an inert atmosphere as the hot aqueous solution oxidises in air. Light brown prisms, m.p. (decomp.) 170°. Sparingly soluble in water and organic solvents, soluble in dilute acids and alkalis.

Both the *arsenoxide* (*Mapharsen*),

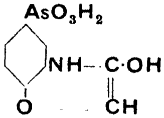
$$(OH)\,(NH_2)C_6H_3{\cdot}AsO,$$

and the *dichloroarsine* (*Halarsol*) have been used in tropical diseases ; the latter is especially useful in the treatment of yaws, while its toxic effects are inconsiderable.

3-*Acetylamino*-4-*hydroxyphenylarsonic acid* (*Stovarsol, Spirocide, Acetarsol*) is produced by heating the amino acid in aqueous suspension with acetic anhydride at 55°. Any free amine is removed with dilute acid and the product purified through the sodium salt. Short colourless prisms, m.p. (decomp.) 240°–250° (Raiziss and Gavron, J. Amer. Chem. Soc. 1921, **43**, 583 ; Christiansen, *ibid.* 1922, **44**, 2340 ; Fourneau, Trefoul, and Bénoit, Bull. Soc. chim. 1927 [iv], **41**, 499). Stovarsol has no trypanocidal activity but it is a valuable drug in the treatment both of amœbiasis and of syphilis. It can be administered orally and hence is particularly useful in infantile syphilis. The *sodium* (*acetarsone*), *calcium* (*realphene*), and *bismuth* (*bistovol*) salts have also been used.

Other acyl derivatives, *e.g.* formyl, crotonyl, etc., have been also tried. The latter compound is said to be less toxic than the others (U.S.P. 1903645 ; G.P. 581329).

3-*Hydroxy*-1 : 4-*benzisooxazine*-6-*arsonic acid*,



Obtained by the action of chloroacetyl chloride on 3-amino-4-hydroxyphenylarsonic acid in the presence of sodium hydroxide or by the diazo synthesis on 6-amino-3-hydroxy-1 : 4-benz*iso*oxazine. Crystallising from hot aqueous solution in rhombs, it is insoluble in cold water, dilute acids, and organic solvents, but dissolves in dilute alkalis.

Reduction of the sodium salt with sodium hyposulphite and magnesium chloride produces 3-3′-*dihydroxy*-6 : 6′-*arseno* 1 : 4-*benzisooxazine*.

Many derivatives of 1 : 4-benz*iso*oxazinearsonic acid have been made and they are pharmacologically interesting in that the minimum curative dose administered orally is of the same order as when injected. Generally the oral dose required is considerably larger than the injected dose (Newbery, Phillips, and Stickings, J.C.S. 1928, 3051 ; Sweet and Hamilton, J. Amer. Chem. Soc. 1934, **56**, 2409 ; G.P. 563397).

Benz*iso*oxazinearsonic acids have also been produced from 4-amino-3-hydroxy- and 2-amino-3-hydroxyphenylarsonic acids (Newbery and others, *l.c.* ; Balaban, *ibid.* 1928, 3066).

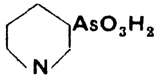
4-*Amino*-2-*hydroxyphenylarsonic acid* (Bauer, Ber. 1915, **48**, 1579 ; Hewitt and King, J.C.S. 1926, 824). Obtained by converting 3-nitro-6-aminophenol into 4-nitro-2-hydroxyphenylarsonic acid and reducing the latter with iron filings and dilute acetic acid or with ferrous chloride. Crystallised from water it melts at 173°.

The *acetylamino* and *formylamino* derivatives (Fourneau, 270 and 417) as well as the unsubstituted product have been used in trypanosomiasis.

Pyridinearsonic Acids.

The pyridinearsonic acids have some therapeutic importance and have been the subject of much study by Binz and his co-workers. They may be obtained through the diazo synthesis, though the yields are not good unless the pyridine has a negative group in the 2-position, the diazo group occupying the 3- or 5-position. Direct arsenation has also been accomplished. The acids are usually purified by oxidising back to the arsenopyridines followed by re-oxidation to the acids. When the 2-position in the nucleus is occupied by a hydroxyl group the compounds generally exhibit the pyridone rather than the hydroxypyridine structure.

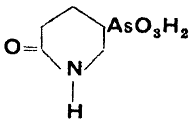
Pyridine-3-*arsonic acid,*



The Bart reaction on 2-chloro-5-aminopyridine yields 2-*chloropyridine*-5-*arsonic acid* which, when heated with an aqueous solution of hydrazine hydrate forms 2-*hydrazinopyridine*-5-*arsonic acid* and this on oxidation with hydrogen peroxide gives pyridine-3-arsonic acid, m.p. 112°–113°; it is insoluble in alcohol, acetone, or ether (Binz and Räth, Annalen, 1927, **455**, 127; Binz, Räth, and Gante, *ibid.* 1928, **467**, 11).

The above acid has also been made by McCleland and Wilson (J.C.S. 1932, 1497) by heating 3-chloromercuripyridine, C_5H_4NClHg, with arsenic trichloride. The resulting 3-*pyridyldichloroarsine hydrochloride* is reduced to the *arsenopyridine* which is reoxidised to the arsonic acid; white prisms from alcohol, m.p. 158°–159°. This product differs considerably from that obtained by Binz but is identical with that prepared from 3-aminopyridine by the diazo process (Binz and von Schickh, Ber. 1936, **69**, 1527).

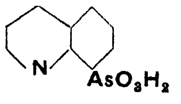
2-*Pyridone*-5-*arsonic acid* (Na salt=*B.R.*1),



As indicated above, the arsenical made from 5-amino-2-hydroxypyrine is not the 2-hydroxypyridine arsonic acid but the isomeric 2-pyridone 5-arsonic acid. If, however, 2-pyridone is fused with arsenic acid for 5 hours then a mixture of the pyridone and hydroxypyridine acids results. All attempts to isolate the hydroxy compound from this mixture have failed, only the pyridone-arsonic acid being obtained. This acid forms white needles sparingly soluble in water and having no melting-point. It has a low toxicity and is well tolerated (Binz, Räth, and Maier-Bode, Annalen, 1930, **478**, 22).

Quinolinarsonic Acids.

Quinoline-8-*arsonic acid,*



Obtained in the usual manner from 8-aminoquinoline and isolated through the *arsenoquinoline*; crystallises in white needles, m.p. 230°, is readily soluble in dilute alkalis and concentrated mineral acids, but insoluble in dilute acids, alcohol and water.

The intermediate 8 : 8′-*arsenoquinoline dihydrochloride* is a yellowish-red powder soluble only in concentrated hydrochloric acid.

The *arsenoxide*, *dichloroarsine hydrochloride*, and the *arsine*, $C_9H_6NAsH_2$, are also known (Binz and Räth, Annalen, 1927, **453**, 238; Slater, J.C.S. 1932, 2104, 2196; Barnett, Gillieson, and Kermack, *ibid.* 1934, 433).

Aryl Thioarsinites.

As indicated in the introductory section the quinquevalent arsonic acids become therapeutically active only on reduction, in the body, to the tervalent state. It might seem natural, therefore, to reduce the acids first and to inject the reduced products. Unfortunately, the difficulty has been to obtain easily soluble and stable derivatives of these tervalent compounds. The most successful substances of this kind are the thioarsinites produced by the interaction of aliphatic or aromatic thiols on arsenoxides, dichloroarsines, or on the arsonic acids themselves. Such sulphur compounds are of interest because of the important part they probably play in actual trypanocidal action.

In general these thioarsinites are stable to acids and are not appreciably hydrolysed in aqueous or sodium bicarbonate solution. They are oxidised by iodine to the arsonic acid and the disulphide, *e.g.*

$$PhAs(SR)_2+2I_2+3H_2O$$
$$=PhAsO_3H_2+4HI+RS{\cdot}SR$$

Thiolacetamide and thiophenol have been suggested as a means of identifying arsonic acids for the resulting thioarsinites are well characterised products (Barber, J.C.S. 1929, 1024; Binz, Räth, and Maier-Bode, *l.c.*).

Di(*carboxymethyl*)-4-*aminophenyl thioarsinite,*

$$NH_2{\cdot}C_6H_4{\cdot}As(S{\cdot}CH_2{\cdot}COOH)_2,$$

p-Arsanilic acid (2·2 g.) is added to a neutral solution of thiolacetic acid (3·8 g.) in 40 c.c. of *N*-sodium hydroxide, when the arsonic acid dissolves, the solution maintaining its neutrality, After acidification with acetic acid the thioarsinite separates in needles sparingly soluble in cold water, readily soluble in hot water and glacial acetic acid, m.p. 142°–143°. The equation for the reaction is :

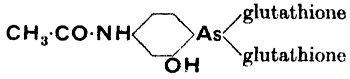
$$NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2+4SH{\cdot}CH_2{\cdot}COOH$$
$$=NH_2{\cdot}C_6H_4{\cdot}As(S{\cdot}CH_2{\cdot}COOH)_2$$
$$+(-S{\cdot}CH_2{\cdot}COOH)_2+3H_2O$$

Di-(*β*-*amino*-*β*-*carboxyethyl*) *benzamide*-p-*thioarsinite,*

$$NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}As[S{\cdot}CH_2{\cdot}CH(NH)_2COOH]_2$$

A mixture of cysteine hydrochloride, dilute sodium bicarbonate, and benzamide-*p*-arsenoxide is boiled for a few minutes and the clear solution made weakly acid to Congo paper. A heavy precipitate is obtained, which on reprecipitation from dilute solution, separates in long needles, decomposing at 240°, sparingly soluble in organic solvents.

Diglutathione-4-acetamino-2-hydroxyphenylthioarsinite,



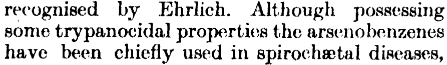
Prepared by treating 4-acetamino-2-hydroxyphenylarsenoxide with an aqueous solution of glutathione, concentrating over sulphuric acid, and finally precipitating with alcohol ; white, amorphous powder which tenaciously retains water. Both this and the preceding compound have a powerful trypanocidal action (Cohen, King, and Strangeways, J.C.S. 1931, 3055 ; 1932, 2505).

ARSENOBENZENES.

The arsenobenzenes are tervalent arsenicals containing the group —As=As—. The parent substance, $C_6H_5·As=As·C_6H_5$, was first made by Michaelis and Schulte in 1881, but the therapeutic importance of this series was first recognised by Ehrlich. Although possessing some trypanocidal properties the arsenobenzenes have been chiefly used in spirochætal diseases, especially syphilis. In the treatment of this latter disease mercurial or, more recently, bismuthial drugs are used in conjunction with the arsenicals, while complex arseno-stibino and arseno-bismutho compounds are also said to have given promising results.

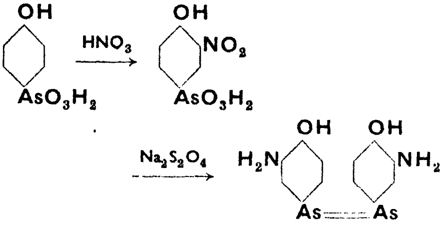
The arsenobenzenes are usually obtained either by the reduction of the corresponding arsonic acids and arsenoxides or by the interaction of a primary arsine with an arsenoxide or chloroarsine. They are solid, sometimes crystalline substances generally possessing a yellow colour ; they regenerate the arsonic acids on oxidation and the double bond is also ruptured on treatment with halogens, alkyl iodides, and sulphur ; co-ordination compounds are formed with the salts of copper, silver, gold, mercury, etc.

p-*Arsenophenylglycine* (Na salt=*Spirarsyl Ehrlich* 418).



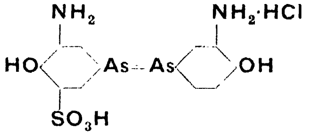
Reddish brown powder, easily soluble in aqueous sodium carbonate, aniline and pyridine ; insoluble in dilute mineral acids, alcohol and benzene. The *sodium* salt is yellow and gives a neutral solution in water. It possesses both trypanocidal and spirillicidal activity.

3 : 3′ - *Diamino* - 4 : 4′ - *dihydroxyarsenobenzene* (Dihydrochloride=*Salvarsan, 606, Arsphenamine, Kharsivan, Arsenobillon*).—Usually prepared from *p*-hydroxyphenylarsonic acid which is successively nitrated and reduced with alkaline sodium hyposulphite and magnesium chloride (G.P. 271894 ; Ehrlich and Bertheim *l.c.* ; Kober, J. Amer. Chem. Soc. 1919, **41**, 442).



The salvarsan base is converted into the *dihydrochloride* by dissolving in methyl alcohol and adding methyl alcoholic hydrochloric acid and ether. Obtained thus, the product often contains methyl alcohol, which is toxic. To avoid this contamination the base is now generally dissolved in sodium hydroxide, the solution filtered, treated with dilute hydrochloric acid, and the hydrochloride precipitated with excess of the concentrated acid. The product is dried over calcium chloride and sodium hydroxide.

Reduced with hyposulphite the salvarsan always contains sulphur-bearing impurities which are not easily removed. The main impurity is 3 : 3′-*diamino*-4 : 4′-*dihydroxy*-5-*sulphoarsenobenzene hydrochloride.*



This has been synthesised by reducing a mixture of 3-amino-4-hydroxy-5-sulphophenylarsonic acid and 3-amino-4-hydroxyphenylarsonic acid with hypophosphorous acid (King, J.C.S. 1921, **119**, 1107, 1420).

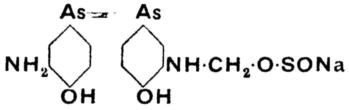
Christiansen has also shown that there are other sulphur impurities which, unlike the foregoing, are soluble in methyl alcohol and do not appreciably increase the toxicity of salvarsan (J. Amer. Chem. Soc. 1922, **44**, 847, 854, 2334 ; 1923, **45**, 1316).

To avoid these by-products, other methods of reducing the nitrohydroxyphenylarsonic acid have been suggested, including an electrolytic process using a mercury cathode, the acid being reduced in the presence of hydrochloric acid and in an inert atmosphere. According to the strength of the acid there is obtained either salvarsan or 3-amino-4-hydroxyphenylarsine hydrochloride (Matsumiya and Nakata, Mem. Coll. Sci. Kyoto, 1927, **10**, 199).

For other methods of synthesising this drug, *see* Bart, Annalen, 1922, **429**, 113 ; Fargher and Pyman, J.C.S. 1920, **117**, 376 ; Karrer, Ber. 1913, **46**, 515.

In its purest form salvarsan base is a pale yellow powder soluble in dilute acids and alkalis. The hydrochloride is practically colourless and dissolves in 5 parts of water to form a gel. The free base, being insoluble in water, cannot be used therapeutically, while the hydrochloride suffers from the disadvantage that its solution has to be treated with sodium hydroxide before injection. Much attention has therefore been given to the production of derivatives soluble in water to neutral solutions.

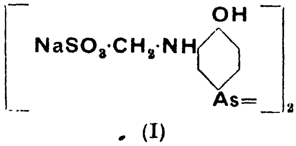
Neosalvarsan (Syn. *Ehrlich* 914, *Neoarsphenamine, Neokharsivan, Novarsenobenzene, Novarsenobillon* (N.A.B.)). This search for a soluble product led Ehrlich to condense salvarsan with sodium formaldehydesulphoxylate whereby such a product is obtained (Chem.-Ztg. 1912, 637 ; G.P. 245756, 263460, 264014, 271893). This substance has been stated to be sodium 3 : 3'-*diamino*-4 : 4'-*dihydroxyarsenobenzene*-N-*methylenesulphoxylate*.



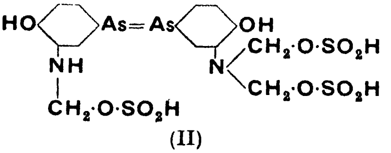
The commercial preparations vary considerably in their analyses, most of them showing a ratio of 2 : 2 for As : S. In addition, there is always present a small amount of sulphate (Dyke and King, J.C.S. 1934, 1707). Neosalvarsan is a pale yellow solid soluble to an almost neutral aqueous solution which rapidly absorbs oxygen on exposure to air.

Sulpharsphenamine (Syn. *Kharsulphan, Metarsenobillon, Myosalvarsan*).—Salvarsan in aqueous-alcoholic solution is treated with formaldehyde and sodium bisulphite ; the yellow precipitate first formed gradually redissolves and, after filtration, the product is precipitated with alcohol. It is a light yellow powder which can be further purified, but even so it is not a pure compound.

Like many of these drugs the constitution of sulpharsphenamine is somewhat doubtful : Voegtlin and Johnson believed it to be 3 : 3'-*diamino* - 4 : 4' - *dihydroxyarsenobenzene* - N : N' - *dimethylene-sulphite* (I). More recently Dyke and King have adduced evidence that the commercial product corresponds to a sodium salt of the N : N : N'-*trimethylene sulphurous acid* (II) (Voegtlin and Johnson, J. Amer. Chem. Soc. 1922, **44**, 2573 ; Christiansen, *ibid.* 1923, **45**, 2184 ; Newbery and Phillips, J.C.S. 1928, 116 ; Dyke and King, *ibid.* 1935, 805).

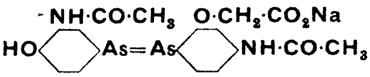


(I)



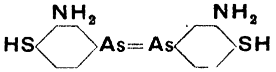
(II)

Although both neo- and sulph-arsphenamine have the advantage over salvarsan in that they are ready for use merely on dissolving in sterile water, yet these solutions do not keep. Compounds have therefore been sought which would be stable in solution and which could be marketed as such. Two preparations of this kind are *Stabilarsan* and *Solusalvarsan.* The former is a di-*N*-glucoside of salvarsan (Anderson, J.S.C.I. 1923, 345), while the latter is *sodium* 3 : 4'-*diacetamino*-4-*hydroxyarsenobenzene*-2'-*glycollate* (B.P. 360957).



The introduction of the glycollic acid radical into arsenobenzenes has had a considerable vogue in recent times. If any amino groups present are acylated such compounds form sodium salts the aqueous solutions of which are stable and neutral and may be injected intravenously, intramuscularly, and subcutaneously (B.P. 400766, 413497 ; G.P. 554951, 560218, 565414).

3 : 3'-*Diamino*-4 : 4'-*dithiolarsenobenzene*,



This thiol analogue of salvarsan has been obtained by the reduction of 3-*nitro*-4-*thiolphenylarsenic disulphide*,

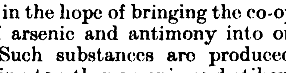
$$HS{\cdot}C_6H_3(NO_2)AsS_2,$$

which, in turn, is formed by treating 4-chloro-3-nitrophenylarsonic acid with potassium hydrosulphide. The arsenobenzene is a yellow amorphous powder, insoluble in acids but soluble in sodium hydroxide to a pale yellow solution (Barber, J.C.S. 1931, 255).

ARSENO-STIBINOBENZENES.

Antimony has often a strong synergistic action on arsenical drugs, as is seen in the increased trypanocidal efficiency of atoxyl when administered along with tartar emetic or other antimony preparations. Consequently, a large number of arseno-stibinobenzenes have been prepared in the hope of bringing the co-operative effects of arsenic and antimony into one compound. Such substances are produced either by reducing together arsonic and stibonic acids or by acting on stibine oxides or dihalides with aromatic arsines. Some of these preparations are stated to have very high chemotherapeutic indices.

3 : 3'-*Diamino*-4 : 4'-*dihydroxyarsenostibinobenzene*,

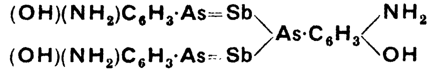


Equimolecular proportions of 3-nitro-4-hydroxyphenyl-arsonic and -stibonic acids, as solutions of the sodium salts, are reduced with sodium hyposulphite. The base separates gradually as an amorphous brown powder and is filtered, washed, and dried in an inert atmosphere. It is insoluble in water, but the *dihydrochloride*, a brownish-yellow powder, dissolves to an acid solution.

The same substance is obtained by the interaction of 3-amino-4-hydroxyphenylarsine and

3-amino-4-hydroxyphenylstibine dichloride (B.P. 178824 ; U.S.P. 1422294 ; Ehrlich and Karrer, Ber. 1913, **46**, 3567 ; Schmidt, Annalen, 1920, **421**, 232 ; G.P. 396697).

Even more complex arseno-antimony compounds are produced by acting on aryl arsines with antimony trichloride, tartar emetic or other antimonyl derivatives. Thus, 3-amino-4-hydroxyphenylarsine and potassium antimonyl-1 : 2-dihydroxybenzene-3 : 5-disulphonate give a product to which the following formula has been assigned:



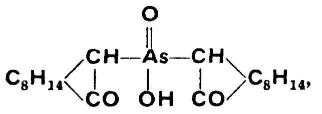
$$\begin{matrix}(OH)(NH_2)C_6H_3\cdot As{=}Sb \\ (OH)(NH_2)C_6H_3\cdot As{=}Sb\end{matrix}\Big\rangle As\cdot C_6H_3\Big\langle\begin{matrix}NH_2 \\ OH\end{matrix}$$

Such substances may be rendered water-soluble by treating with formaldehyde bisulphite or formaldehydesulphoxylate.

Similar complex arseno-arsenic and arseno-bismuth derivatives have also been made (G.P. 573538, 567275 ; B.P. 388054 ; U.S.P. 2052670).

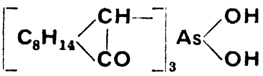
Miscellaneous Organic Compounds of Arsenic.

Dicamphorylarsinic acid,



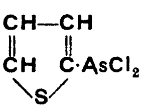
a condensation product from sodium, camphor, and arsenic trichloride, forms colourless transparent prisms ; m.p. 266° (with decomp.) ; $[\alpha]_D^{20}+186\cdot6°$; practically insoluble in water or petroleum, more soluble in benzene, freely soluble in chloroform and alcohol (Morgan and Micklethwait, J.C.S. 1908, **93**, 2146 ; 1909, **95**, 1476 ; Morgan and Moore, J.C.S. 1910, **97**, 1699).

Tricamphorylarsine dihydroxide,

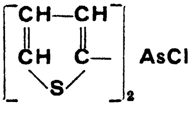


is obtained from the final mother liquors of the above preparation after fractionation, the product being a brown amorphous solid very soluble in benzene, alcohol or acetic acid (Morgan and Micklethwait, *l.c.*).

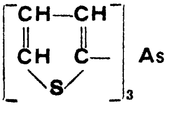
Thienyldichloroarsine (I), *Dithienylchloroarsine* (II), and *Trithienylarsine* (III).



(I)



(II)

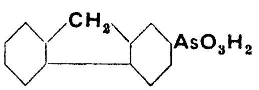


(III)

These are obtained as successive fractions from the filtrate when arsenious chloride and mercuridithienyl are allowed to react under carefully regulated conditions (Steinkopf, with Bauermeister, Annalen, 1917, **413**, 331).

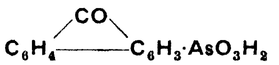
This reaction was first studied by Finzi and Furlotti (Gazzetta, 1915, ii, **45**, 280), who also oxidised the two chloro compounds to the corresponding *thienylarsonic* and *dithienylarsinic acids.* Finzi has since prepared a number of these thienyl arsenicals, including several arsenothiophens (*ibid.* 1925, **55**, 824 ; 1930, **60**, 159 ; 1932, **62**, 244).

Fluorene-2-arsonic acid,



Obtained from 2-aminofluorene by the diazo method ; sparingly soluble white needles from hot alcohol. It forms only a *monosodium salt* crystallising from hot water in colourless plates with 1 mol. H_2O. 2-*Dichloroarsinofluorene*, colourless needles, m.p. 109°.

Fluorenone-2-arsonic acid,

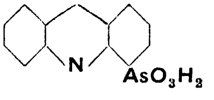


$$C_6H_4\overset{CO}{\text{——}}C_6H_3\cdot AsO_3H_2$$

Prepared from 2-aminofluorenone as yellow needles and forming a *mono-* and *di-sodium salt.* 2-*Dichloroarsinofluorenone*, bright yellow plates, m.p. 142°.

Nitration of the above acid followed by reduction yields 7-*aminofluorenone*-2-*arsonic acid* from which several derivatives have been made by substituting in the amino group (Morgan and Stewart, J.C.S. 1931, 620 ; 1932, 1634 ; 1933, 1454 ; Cislak and Hamilton, J. Amer. Chem. Soc. 1931, **53**, 746).

1-*Acridylarsonic acid,*



Obtained by the Bart reaction on 1-aminoacridine sulphate in acetic acid or after diazotising 1-amino-9 : 10-dihydroacridine with excess of sodium nitrite. The *hydrochloride* forms yellow crystals, m.p. 302°–303° (with decomp.), only slightly soluble in water and insoluble in alcohol. The solution in sulphuric acid shows a green fluorescence. The corresponding *dichloroarsine hydrochloride* and *oxide* have been made.

Similarly there have been prepared the 2- and 3-*acridylarsonic* acids as well as *acridone*-3-*arsonic acid* (Sherlin and others, Annalen, 1935, **516**, 218 ; Barnett, Gillieson, and Kermack, J.C.S. 1934, 433).

Arsonic acids containing the furan, carbazole or coumarin nuclei have also been made (Lowe and Hamilton, J. Amer. Chem. Soc. 1935, **57**, 1081, 2314 ; Scherlin and Berlin, J. Gen. Chem. Russ. 1935, **5**, 938 ; Burton and Gibson, J.C.S. 1927, 2386 ; Goswami and Das-Gupta, J. Ind. Chem. Soc. 1931, **8**, 417 ; 1932, **9**, 91).

Diphenylamine and triphenylamine arsonic acids.—The diphenylaminearsonic acids are produced either by the interaction of a bromoarylarsonic acid with an arylamine, or from an aminoarylarsonic acid and a bromobenzene. Direct arsenation may also serve in certain cases. These acids are of interest because of their relationship with the phenarsazines.

Diphenylamine-o-*arsonic acid*,

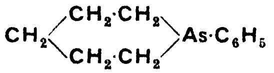
$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2,$$

is obtained when aniline and *o*-bromophenylarsonic acid are boiled in amyl alcohol for 5 hours with dry potassium carbonate and a little copper powder. Alternatively, arsanilic acid and bromobenzene may be used, though in this case, if the reaction temperature is too high, *triphenylamine*-o-*arsonic acid* is also formed.

Diphenylamine-*o*-arsonic acid forms colourless needles, m.p. 166° (slight decomposition); insoluble in ether, chloroform or benzene, easily soluble in alcohols, acetone and ethyl acetate. The yellowish-green solution in nitric acid becomes deep red on adding concentrated sulphuric acid (Gibson and Johnson, J.C.S. 1927, 2499; Wintersteiner and Lieb, Ber. 1928, **61** [B], 1126; U.S.P. 1997304).

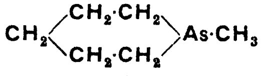
CYCLIC DERIVATIVES OF ARSENIC.

Cyclic arsenicals were first obtained by Grüttner and Wiernik, who prepared *phenyl*-cyclo*pentamethylenearsine* (I). Soon after, Zappi made the simpler *methyl* derivative (II) together with many other similar substances. The general method of synthesis is through the agency of the Grignard reaction. Both these substances are colourless oils and they exhibit the usual properties of trivalent arsenicals. The *dichloride* of (II) when heated *in vacuo* yields cyclo-*pentamethylene-chloroarsine*, m.p. 26°–27°, from which the corresponding *oxide* and *arsonic acid* have been made (Grüttner and Wiernik, Ber. 1915, **48**, 1473; Zappi, Bull. Soc. chim. 1916 [IV], **19**, 151, 290; 1931 [IV], **49**, 366; Gorski and Schpanski, J. Gen. Chem. Russ. 1934, **4**, 1270, 1283).



$$CH_2\!\left\langle\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\right\rangle\!As{\cdot}C_6H_5$$

(I)

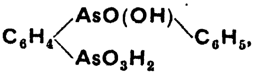


$$CH_2\!\left\langle\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\right\rangle\!As{\cdot}CH_3$$

(II)

In more recent times many arsenical analogues of heterocyclic nitrogen compounds have been made and some of them, especially the phenarsazines, have been closely studied.

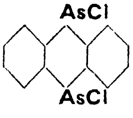
Arsanthrene chloride (I).—*Phenylarsinophenyl*-o-*arsonic acid*,



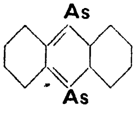
$$C_6H_4\!\left\langle\begin{matrix}AsO(OH)\\AsO_3H_2\end{matrix}\right.\!\!\!\!\!\!\!\!\!\diagdown C_6H_5,$$

obtained by the action of phenylarsenoxide on diazotised *o*-arsanilic acid, undergoes ring closure when reduced with sulphur dioxide in concentrated hydrochloric acid, giving the chloride (I); lanceolate crystals, m.p. 182°–183°, easily soluble in chloroform, benzene, and carbon disulphide; sparingly soluble in alcohol. Oxidised by nitric acid (*d* 1·38) it forms *arsanthrenic acid*.

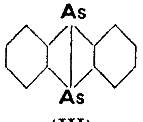
Arsanthrene (II) or (III).—This arsine results when the chloride is reduced with zinc and hydrochloric acid or when the *oxide* is boiled with phenylhydrazine; it forms orange-yellow rhombic plates which darken on heating and melt at 340°–350°. Slightly soluble in boiling acetic acid, pyridine, or phenylhydrazine; insoluble in other solvents.



(I)



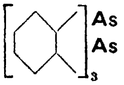
(II)



(III)

(Wieland and Rheinheimer, Annalen, 1921, **423**, 31; Kalb, *ibid.* 39.)

Arsanthrene oxide when distilled in carbon dioxide under slightly reduced pressure sheds arsenious oxide and forms *tri*-o-*phenylene diarsine*,



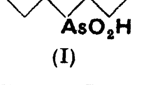
as a colourless crystalline substance, m.p. 295°–296° (McCleland and Whitworth, J.C.S. 1927, 2753).

Xenylene-2 : 2′-*arsinic acid* (I) is produced when *xenyl*-o-*arsonic acid*,

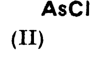
$$C_6H_5{\cdot}C_6H_4{\cdot}AsO_3H_2,$$

is warmed for a few minutes with concentrated sulphuric acid and the solution poured into water. Recrystallised from hot water it melts at 290°.

Xenylene-2 : 2′-*chloroarsine* (II).—Obtained from the arsinic acid (I) in the usual manner or by distilling *xenyl*-o-*dichloroarsine* in a vacuum, crystallises from benzene in colourless plates, m.p. 161°. Easily soluble in chloroform, less so in benzene or alcohol. The *iodide*, m.p. 166°, forms golden plates, and with the Grignard reagent gives *xenylene*-2 : 2′-*methylarsine* as large transparent prisms, m.p. 46°.



(I)

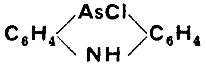


(II)

(Aeschlimann, Lees, McCleland, and Nicklin, J.C.S. 1925, 66; Razuvaiev and Koton, J. Gen. Chem. Russ. 1932, **2**, 889.)

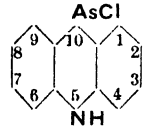
By similar methods there have been obtained 10-*chloro*-5 : 10-*dihydroacridarsine*, 10-*chlorophenthiarsine*, and 10-*chlorophenoxarsine*.

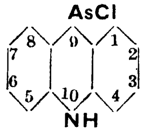
PHENARSAZINES.—These arsenicals, first investigated during the Great War, have been the subject of considerable research, especially by Gibson and his co-workers in England and by Razuvaiev in Russia. The simplest member, *phenarsazine chloride*, was produced in 1913 by heating diphenylamine with arsenious chloride and was given the formula



$$C_6H_4{<}\begin{matrix}\mathrm{AsCl}\\ \mathrm{NH}\end{matrix}{>}C_6H_4$$

Since then a number of derivatives have been made. Two systems of nomenclature have been used for the substances as indicated below; the English and American journals have advocated the first, while the German Chemical Society has adopted the second.

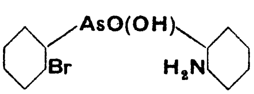




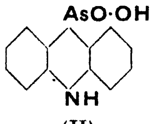
Phenarsazine chloride (*10-chloro-5 : 10-dihydrophenarsazine*).—Originally prepared as above, has also been obtained in many other ways. When pure it is a bright yellow crystalline compound, m.p. 191°–192°, and can be sublimed *in vacuo*. Its solution in concentrated sulphuric acid is deep red and from it the *sulphate* is deposited on dilution. The chloride is highly reactive and possesses in a marked degree the property of forming additive compounds with a variety of solvents. It reacts with the Grignard reagent to form 10-alkyl (or aryl)-5 : 10-dihydrophenarsazines and these function in the usual manner of tertiary arsenicals, forming arsonium iodides with alkyl iodides and being oxidised by alcoholic iodine to oxides and hydroxides (Wieland and Rheinheimer, Annalen, 1921, **423**, 1; Seide and Gorski, Ber. 1929, **62**, 2186; Razuvaiev and Malinovski, Ber. 1931, **64**, 120; J. Gen. Chem. Russ. 1935, **5**, 570).

The constitution of phenarsazine chloride is established by the following synthesis due to Burton and Gibson (J.C.S. 1926, 452).

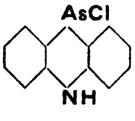
o-Bromophenylarsenoxide, coupled with diazotised *o*-nitroaniline gives 2-bromo-6′-nitrodiphenylarsinic acid which is reduced with ferrous hydroxide to the amine (I). This on heating in amyl alcohol with potassium carbonate and a trace of copper powder yields phenarsazinic acid (II), from which the chloride (III) is obtained in the usual manner. Actually, Gibson believes that although the chloride can function according to (III) it most often possesses the transannular bond structure (IV).



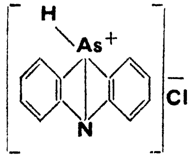
(I)



(II)



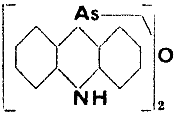
(III)



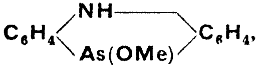
(IV)

The method of direct arsenation, while applicable in many cases, fails when the diphenylamine nucleus contains strongly negative groups such as nitroxyl or carboxyl. Hence a general method of synthesis has been devised which consists in cyclicising diphenyl-amino-*o*-arsonic acids. The ring closure is either produced by boiling the acids with hydrochloric acid or by reduction with sulphur dioxide in the presence of the same mineral acid (Burton and Gibson, J.C.S. 1927, 247; Gibson and Johnson, *ibid.* 2499).

10 : 10′-*Oxybis* (5 : 10-*dihydrophenarsazine*),



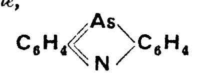
is obtained either by the action of alkalis on phenarsazine halides or by heating diphenylamine with arsenious oxide and phosphorus pentoxide at 160°–170°, colourless plates, m.p. 350°; it forms ethers with alcohols and phenols, the *methyl ether*,



$$C_6H_4{<}\begin{matrix}\mathrm{NH}\\ \mathrm{As(OMe)}\end{matrix}{>}C_6H_4,$$

crystallising in long needles, m.p. 194°.

Phenarsazine,

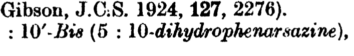


$$C_6H_4{\ll}\begin{matrix}\mathrm{As}\\ \mathrm{N}\end{matrix}{>}C_6H_4$$

This, the parent substance of the series, is formed when the above methyl ether is boiled with diphenylmethylamine in an atmosphere of carbon dioxide; orange-red prisms, m.p. about 310°. Its solutions are highly coloured but are decolorised almost immediately in air, the oxide being formed. Phenarsazine is very reactive and unites readily with alcohols, phenols, amines, acetic acid and hydrochloric acid (Wieland and Rheinheimer, *l.c.*).

Phenarsazinic acid, obtained as above or when the oxide or chloride is oxidised, crystallises from acetone in needles, m.p. above 300°; it is amphoteric, forming salts with alkalis and acids (Wieland and Rheinheimer, *l.c.*; Burton and Gibson, J.C.S. 1924, **127**, 2276).

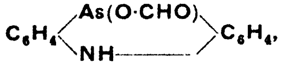
10 : 10′-*Bis* (5 : 10-*dihydrophenarsazine*),



$$NH{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}As{-}As{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}NH$$

Prepared by reducing phenarsazine chloride or the acid with hypophosphorous acid; orange-yellow needles, m.p. 304°–305° (with decomp.), it is sparingly soluble in the usual solvents and easily oxidised to phenarsazinic acid when boiled with acetone or xylene. With bromine in carbon tetrachloride it forms phenarsazine bromide (Burton and Gibson, J.C.S. 1926, 2244).

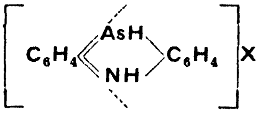
5 : 10-*Dihydrophenarsazine formate*,



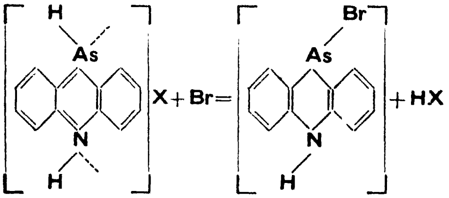
$$C_6H_4{<}\begin{matrix}\mathrm{As(O{\cdot}CHO)}\\ \mathrm{NH}\end{matrix}{>}C_6H_4,$$

is formed when 10 : 10′-oxy-bis (5 : 10-dihydrophenarsazine), 10-methoxy-5 : 10-dihydrophenarsazine, or certain other derivatives are treated with formic acid in a suitable solvent. As the formate is unstable in air, the solvent is removed *in vacuo* over potassium hydroxide, when colourless needles are obtained which darken at 100°–110°, become intensely yellow at 130°, and melt (decomp.) at 315°–320° (Razubaiev, Ber. 1929, **62**, 605 ; Gibson, Johnson and Vining, Rec. trav. chim. 1930, **49**, 1029).

The action of formic acid on phenarsazines is especially interesting. In the cold only a faint yellow solution is produced, but this, on warming, becomes intensely red ; the colour is discharged on cooling and shaking, but reappears on further warming. The above formate gives no colour when warmed in acetone solution, though the colour does appear on adding formic acid. Similar results are obtained with other reducing agents, but in these cases the reduction proceeds a step further, and a colourless solution is finally obtained which re-develops the red colour on exposure to air. It has been shown that one atom of hydrogen is used up per molecule of the arsazine in the production of the coloured compound which would correspond to a quinhydrone structure for this substance. Its unsaturated character (adding on Cl, Br, I, O, NO, NO_2) and its high electrical conductivity have, however, led Razubaiev to assign to it the meriquinonoid structure of a half-free radical,

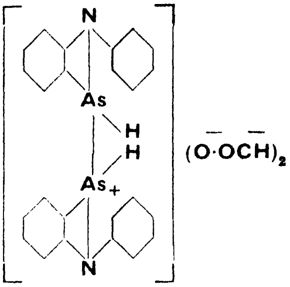


This compound adds on, with decolorisation, 1 atom of halogen, but the addition product has not been isolated, there being obtained a theoretical yield of 10-halogeno-5 : 10-dihydrophenarsazine irrespective of the nature of the anion X.



The hydrogen is very loosely attached to the arsenic and may readily be removed by oxygen or sulphur with the production of water or hydrogen sulphide.

Gibson, Johnson, and Vining (*l.c.*), who have also studied the action of formic acid on 10 : 10′-oxybis (5 : 10-dihydrophenarsazine), dissent from the above views and offer alternative suggestions. These authors believe that the heterocyclic ring is opened during the reaction and that the crimson-coloured compound has the following constitution :



(Razubaiev, Ber. 1929, **62**, 605, 1208, 2675 ; 1930, **63**, 343 ; Rec. trav. chim. 1931, **50**, 900 ; J. Gen. Chem. Russ. 1934, **4**, 629).

Bibliography.—" Text-Book of Inorganic Chemistry," Vol. XI, Part II, A. E. Goddard, London, 1930 ; " Recent Advances in Chemotherapy," G. M. Findlay, London, 1930 ; " Organic Arsenical Compounds," Raiziss and Gavron, New York, 1923 ; " Organic Compounds of Arsenic and Antimony," G. T. Morgan, London, 1918 ; " Handbuch der organischen Arsenverbindungen," A. Bertheim, Stuttgart, 1913 ; " Die aromatische Arsenverbindungen," H. Schmidt, Berlin, 1912 ; " Die Arzneimittel-Synthese," S. Fraenkel, Berlin, 1912. G. R. D. and G. T. M.

ARSENILLO *v.* ATACAMITE.

ARSENOBILLON (*Salvarsan*) *v.* ARSENICALS, ORGANIC.

ARSENOKLASITE,

$$Mn_3(AsO_4)_2\cdot 2Mn(OH)_2,$$

occurs as red orthorhombic cleavages in manganese ore at Långban, Sweden (G. Aminoff, K. Svenska Vet. Akad. Handl. 1931, **9**, no. 5, p. 52). L. J. S.

ARSENOPYRITE *v.* MISPICKEL.

ARSINE (*Arsenic trihydride*) *v.* ARSENIC.

ARSPHENAMINE (*Salvarsan, 606*) *v.* ARSENICALS, ORGANIC.

ARTABOTRINE, an alkaloid from the bark of *Artabotrys suaveolens* (Marañon, Phil. J. Sci. 1929, **38**, 259), m.p. 187°, is according to Santos and Reyes (Univ. of Philippines Nat. and App. Science Bull. 1932, **2**, 409)

$$C_{17}H_{13}O(OMe)_3\cdot NMe,$$

$[\alpha]_D^{30°}$ +198·7°, and is accompanied by the phenolic alkaloid *suaveoline*,

$$C_{16}H_{10}OH(OMe)_3\cdot NMe,$$

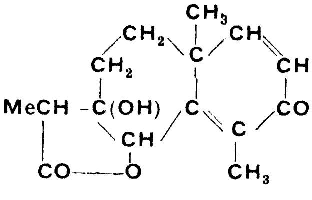
m.p. 182°, $[\alpha]_D^{30°}$ +203·6°. In the writer's laboratory 0·18% of the former and 0·025% of the latter have been isolated, and the impression has been gained that artabotrine is of the oxyacanthene type,

$$C_{32}H_{22}O_2(OMe)_6(NMe)_2,$$

in which the two oxygen atoms form bridges between two benzyl*iso*quinoline residues. G. B.

ARTARINE *v.* ISOQUINOLINE ALKALOIDS.

ARTEMISIN occurs, associated with santonin, in the seeds of *Artemisia maritima*; it forms colourless crystals, m.p. 203°, $[\alpha]_D$ −84·3 (Bertolo, Pharm. J. 1902, 489; Gazzetta, 1923, **53**, 724; 1926, **56**, 856; Freund and Mai, Ber. 1901, **34**, 3717; Wedekind and Koch, Ber. 1905, **38**, 1845). It has been shown by Tettweiler, Engel and Wedekind (Annalen, 1932, **492**, 105) to be 7-hydroxy-santonin.



ARTERENOL. Trade name for 3:4 dihydroxyphenyl-ethanolamine. *v.* ADRENALINE.

ARTHOFORM (new and old) *v.* ANÆSTHETICS.

ARTICHOKE. The name is applied to three distinct varieties of vegetable:

(1) Globe artichoke, the flower head of *Cynara scolymus*.

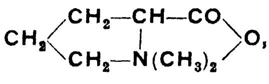
(2) Japanese or Chinese artichoke ("Chorogi"), the tuber of *Stachys tuberifera*,

(3) Jerusalem artichoke, Namara potato, or Topinambur, the tuber of *Helianthus tuberosus*.

Stromer and Stift (Bied. Zentr. **21**, 820) record the following analyses:

	Water.	Carbo-hydrate.	Protein.	Fat.	Ash.
Jerusalem artichoke	79·5	16·7	2·6	0·2	1·0
Japanese artichoke	78·0	14·6	4·3	0·16	1·2
Globe artichoke	85·0	6·8	2·8	1·4	1·1

Stachys tubers contain a variety of protein and amide materials, among which the following have been isolated: glutamine, tyrosine, arginine, choline, trigonelline. Schulze and Trier (Z. physiol. Chem. 1910, **67**, 59) also obtained a characteristic alkaloid *stachydrine* (dimethylbetaine of α-proline),



of which approximately 0·18% occurs in the dry matter of the tubers.

The characteristic carbohydrate is *stachyose*, $C_{24}H_{42}O_{21},4H_2O$, yielding on hydrolysis one molecule of glucose, one molecule of fructose, and two molecules of galactose from one molecule of the carbohydrate.

In the Jerusalem artichoke the customary plant protein matter is accompanied by betaine and the principal carbohydrate is inulin. In the mid-season of growth, leaves and stems contain notable proportions of sucrose, glucose, and fructose, which are steadily translocated to the tubers and stored as inulin during the autumn months. Collins and Gill (J.S.C.I. **1926**, **45**, 63T) have made an extensive examination of the carbohydrate distribution in the tubers and whole plants throughout growth. The following data show values obtained during the actual formation of tubers:

	Oct. 2.	Oct. 30.	Dec. 13.
Total sugar (including inulin)	46·7	52·8	55·3
Reducing sugar	7·0	5·2	8·2
Fructose	6·7	4·8	8·5

(as percentage of the total dry matter).

R. Vardas (Chem.-Ztg. 1934, **58**, 249) also quotes the mature tuber as containing H_2O, 78%; inulin, 16·9%. The tubers contain inulase which converts inulin to fructose, and through the activity of this enzyme alcohol is manufactured from artichoke tubers. The mashed tuber is warmed to 56°–60° for approx. 2 hours during which the inulase action is practically completed. The cooled product is then fermented by yeast. In this way 8–8·5 litres of alcohol are obtained from 100 kg. of tubers. Recently Hardy (Ind. Eng. Chem. 1933, **25**, 1395) has elaborated a process for producing a relatively pure fructose syrup from artichoke juice by electrolysis. The conditions are so adjusted that colloidal matter in the juice is precipitated and removed, and at the same time inulin is hydrolysed to fructose.

The green tops and stems of Jerusalem artichokes have a sufficient nutrient content to serve as cattle feed, provided they are cut sufficiently early in the season. Lüske (Bied. Zentr. 1934, B, **6**, 227) examined the hayed tops with the following results.

	Digestible protein.	Starch equivalent.
Cut in June	1·06%	45·6%
Cut in December	0·36%	19·8%

A. G. Po.

ARTIFICIAL AMBER *v.* BALSAMS.

ARTIFICIAL CAMPHOR *v.* BORNYL CHLORIDE.

ARTIFICIAL TRANSMUTATION *v.* ATOMIC STRUCTURE.

ARTISIL *v.* ACETATE SILK DYES.

ARTOCARPUS INTEGRIFOLIA. *Jack Fruit.* The tree is valued in the E. Indies and Brazil for its edible fruit and for its grained wood. In the latter A. G. Perkin found the yellow dyestuff *morin* (J.C.S. 1895, **67**, 937) and *cyanomaclurin*, $C_{15}H_{12}O_6$ (Proc. Chem. Soc. 1902, **18**, 139; 1904, **20**, 170; 1905, **21**, 160). *A. incisa* is the bread-fruit tree of the Pacific islands. *A. Kunstleri* (Malay), Tutor bark, yields a fibre suitable for paper (B. 1926, 266).

ARUM MACULATUM (Fam. *Araceæ*). *Cuckoo-pint. Lords and Ladies.* The red berries contain an irritant poison, the leaves a saponin and an alkaloid. The enzymes in the buds include an oxydase, an amylase and a protease. None of these constituents have been completely identified (Wehmer, Pflanzenstoffe, I (1929), 135).

ASAFŒTIDA. Asafœtida, a gum resin, containing some essential oil, is an exudation from the rhizome and root of *Ferula fœtida*, *F. rubricaulis*, *F. narthex*, and probably of *F. scorodorma* (Umbelliferæ). The plants are indigenous to Eastern Persia and Western

Afghanistan. It is, to a considerable extent, brought to Bombay, whence it is exported. The drug is obtained by cutting off the stem close to the crown of the root and allowing the exudation to harden. It occurs in flattened tears or in agglutinated masses, has a foul odour, and is commonly called "Devil's Dung." It is used to a small extent in medicine, and in America as a remedy for the so-called "heaves" in horses, and is also used in minute amount in flavouring sauces, many of the well known brands containing a trace of this resin.

It is official in the British Pharmacopœia, which requires it to yield not more than 50% of matter insoluble in alcohol, and not more than 15% of ash.

In spite of numerous statements to the contrary, asafœtida is rarely deliberately adulterated, although an enormous amount of low-grade material is met with, due to the presence of earthy matter and organic debris.

Harrison and Self ("Year Book of Pharmacy," 1912, 420) have given a number of figures for samples of asafœtida, which are certainly the most reliable that have been published. They are as follows :

Nature.	Loss on drying %.	Resin %.	Ash %.	Oil %.	Oil as % of gum resin.	Sp.gr. of oil at 15·5°.	R.I. of oil at 20°.	Rotation of oil.	% S in oil.	S in oil as % of sample.	S in oil as % of gum resin.
Mixed, chiefly soft paste . . .	22·3	50·1	4·3	17·7	18·5	0·929	1·5014	− 0° 11′	22·3	3·95	4·13
Soft paste . .	26·0	41·3	5·6	8·3	8·3	0·943	1·5083	− 10° 20′	27·3	2·27	2·35
Soft paste . .	32·2	52·1	3·9	19·6	20·4	0·919	1·4968	+ 4° 13′	17·3	3·37	3·53
Soft paste . .	24·4	23·9	43·7	5·5	9·8	0·964	1·5124	− 9° 2′	21·7	1·19	2·13
Soft paste . .	18·7	20·9	52·6	5·9	12·4	0·973	1·5130	− 11° 43′	20·7	1·22	2·57
Soft conglomerate . . .	24·0	56·8	2·7	13·9	14·3	0·973	1·5154	− 9° 29′	23·6	3·28	3·37
Dry conglomerate	18·8	54·1	6·2	11·1	11·8	0·918	1·4951	+ 10° 58′	17·1	1·90	2·02
Hard mass . .	7·9	19·4	46·1	4·6	8·5	0·993	1·5259	− 8° 23′	31·4	1·44	2·67
Large tears . .	18·4	50·5	12·3	6·8	7·8	0·959	1·5089	− 10° 23′	21·1	1·43	1·65
Tears . . .	—	—	—	17·1	—	—	1·5078	—	17·5	2·99	—
Tears . . .	—	—	—	20·8	—	—	1·5037	—	8·9	1·85	—

Asafœtida of normal character contains about 25% of gum, from 40 to 64% of resin, and 6 to 17% of essential oil. The resin consists of asaresinotannol partly free and partly combined with ferulic acid.

The acid value of the extracted resin varies between 11 and 82, and the ester value between 82 and 214.

Sechler and Becker (Amer. J. Pharm. 1912, **84**, 4) give the following method for detecting ammoniacum and galbanum in asafœtida.

If 2 c.c. of a 10% emulsion of asafœtida with water be diluted with 5 c.c. of water and floated on to the surface of a solution of sodium hypobromite, an olive-green colour results. In the presence of ammoniacum a transient cherry-red tint is formed. If 2 c.c. of the aqueous emulsion be floated on to cold sulphuric acid there is no perceptible change, but if galbanum be present a violet colour develops.

American chemists have suggested the lead number as a criterion of the quality of asafœtida (*i.e.* the number of milligrams of lead contained in the lead acetate precipitation of 1 g. of the pure resin). According to the United States Customs Authorities this should not be below 200. E. J. Parry (Chemist and Druggist, 1913, **82**, 34) and Harrison and Self (Pharm. Journ. 1913 [4], **36**, 218) have shown that this test is valueless.

Essential oil of asafœtida is a liquid of disgusting odour consisting of terpenes and sulphur compounds, principally $C_7H_{14}S_2$ and $C_{11}H_{20}S_2$, $C_8H_{16}S_2$ and $C_{10}H_{18}S_2$. Its specific gravity varies from 0·915 to 0·993, refractive index 1·4940 to 1·5260, and optical rotation +11° to −36°. E. J. P.

ASARONE, 1 : 2 : 4 : 5-trimethoxypropenylbenzene, $C_6H_2(OMe)_3CH : CHMe$ (Rizza and Boutlerow, J. Russ. Chem. Soc. 1887 **19**, 1 ; Gattermann and Eggers, Ber. 1899, **32**, 289), m.p. 62°, b.p. 296°, d^{11} 1·091, and n_D^{11} 1·5719, occurs naturally in the essential oil of *Asarum arifolium* and to a small extent in matico and acorus oils. It forms a *dibromide*, m.p. 85°–86°, and yields on oxidation *asaraldehyde*,

$$C_6H_2(OMe)_3CHO,$$

m.p. 114° (*oxime*, m.p. 138°), and *asaronic acid* (1 : 3 : 4-trimethoxybenzoic acid), m.p. 144°.

ASARUM CANADENSE (Fam. *Aristolochiaceæ*). A plant indigenous to North America, where it is known by the names of "Wild Ginger," or "Canada Snake-root." The rhizome yields on distillation an essential oil used in perfumery, containing a phenol, $C_9H_{12}O_2$, *d*- and *l*-pinene, *d*-linalool, *l*-borneol, *l*-terpineol, geraniol, eugenol methyl ether, a lactone, $C_{14}H_{20}O_2$, a mixture of fatty acids, including palmitic and acetic, and a blue oil of undetermined composition consisting of oxygenated substances of alcoholic nature (Power and Seed, Chem. Soc. Trans. 1902, **81**, 59).

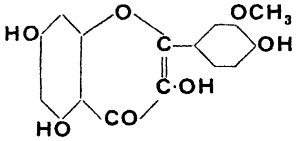
The oil distilled from the rhizomes has d_{15} 0·9516–0·9520 ; α_D −2·50° to −10·42°, and n_D^{20} 1·4850–1·4886 (Gildemeister, "Die ätherischen Oele," 1929, ii, 529). C. T. B.

ASBARG. Asbarg consists of the dried flowers and flowering stems of the *Delphinium zalil*, which is found in great quantity in Afghanistan. The dyestuff was much used in India in silk-dyeing for the production of a sulphur-yellow colour known as "gandkaki," and, together with *Datisca cannabina*, to obtain a similar shade on alum-mordanted silk; it was also used in calico-printing.

The colouring matters of asbarg are present entirely as glucosides, and are best isolated in the crude condition by digesting the boiling aqueous extract with a little sulphuric acid (Perkin and Pilgrim, J.C.S. 1898, **73**, 268). A brownish-yellow powder thus separates, which consists of *iso*rhamnetin, quercetin, and probably kaempferol.

iso*Rhamnetin*, $C_{16}H_{12}O_7$, the sparingly soluble constituent, forms yellow needles resembling rhamnetin in appearance. With lead acetate in alcoholic solution an orange-red precipitate is formed, whilst ferric chloride gives a greenish-black coloration. Fused with alkali, phloroglucinol and protocatechuic acid are produced, and when air is aspirated through its alkaline solution, phloroglucinol and vanillic acid are obtained.

*iso*Rhamnetin gives a *tetra-acetyl* derivative, colourless needles, m.p. 205°–207°; and with methyl iodide a *trimethyl ether* which is identical with quercetin tetramethyl ether. As, moreover, *iso*rhamnetin yields quercetin by demethylation, its constitution can only be represented as follows:



and this has been confirmed by synthesis (Heap and Robinson, J.C.S. 1926, 2336). ω-Benzoyloxyphloracetophenone, when heated with benzoylvanillic anhydride and sodium benzoylvanillate, yields a product, probably a tetrabenzoyltrivanilloyl*iso*rhamnetin, from which *iso*rhamnetin, m.p. 305° (decomp.), is obtained by hydrolysis.

The dyeing properties of *iso*rhamnetin are similar to those of kaempferol (*v.* Delphinium Consolida). *iso*Rhamnetin is also present in yellow wallflowers (*Cheiranthus cheiri*) (Perkin and Hummel, J.C.S. 1896, **69**, 1566), and in red clover flowers (*Trifolium pratense*) (Power and Salway, J.C.S. 1910, **97**, 245).

In dyeing properties asbarg closely resembles quercitron bark (*q.v.*), but yields with aluminium mordant a purer, or less orange, yellow. The colouring matter is present in the flowers, apart from the flowering stalks, to the extent of 3·47%.

The stems and flowers of the *D. saniculæfolium* give shades analogous to, though somewhat weaker than, those yielded by the *D. zalil.*

A. G. P. and E. J. C.

ASBESTINE. Short-fibre asbestos, formerly waste, now added to paints to maintain the pigment in suspension (*cf.* British Standards Specification 255/1926).

ASBESTOS, from ἄσβεστος, "unquenched." Both in ancient and modern times various silicate minerals, closely resembling one another in their finely fibrous texture and flexibility, have been, and are still, confused under this name. The same is true also of the name "amianthus" or "aminatos" (ἀμίαντος, "undefiled," because not injured by fire). They are, therefore, collective names of no more definite signification than the adjective "asbestiform." Some mineralogists limit the name asbestos to the fibrous forms of hornblende but this limitation is not generally observed. Any ambiguity may be avoided by using the terms amphibole-asbestos (or hornblende-asbestos), serpentine-asbestos, etc., for these asbestiform minerals. The finely fibrous texture is, of course, an accidental character of the mineral species, depending on the enormous elongation in one direction of the individual crystals which form the aggregate. Such a character might, indeed, be assumed by many kinds of minerals; but it is only the following that are of any importance in this connection:

Tremolite, $H_2Ca_2Mg_5(SiO_3)_8$.
Actinolite, $H_2Ca_2(Mg,Fe)_5(SiO_3)_8$.
Crocidolite, $H_2Na_2Fe''_3Fe'''_2(SiO_3)_8$.
Anthophyllite, $H_2(Mg,Fe)_7(SiO_3)_8$.
Serpentine, $H_4Mg_3Si_2O_9$.
Palygorskite group (pilolite, etc.), $\left\{\begin{array}{l} nH_2Mg_2Si_3O_9,3H_2O. \\ mH_2Al_2Si_4O_{12},5H_2O. \end{array}\right.$

The first two of these differ only in the relative proportions of the mutually replaceable magnesium and ferrous iron (and consequently also in their colours, which are white and green respectively), and they are varieties of the monoclinic amphibole or hornblende. Crocidolite is a fibrous variety of another species (riebeckite) of the amphibole group of minerals, crystallising in the monoclinic system, and also with an angle of 56° between its prismatic cleavages. It is known in the trade as "blue asbestos," and it gives the name to the Asbestos Mountains in South Africa, where it is found. Anthophyllite also belongs to the amphibole group, but is orthorhombic in crystallisation. Serpentine occurs in nature as large rock-masses, and the compact rock is frequently traversed by veins of fibrous material of the same composition; the latter is known to mineralogists as *chrysotile*, and in the trade as "asbestos" or "Canadian asbestos." In the minerals of the palygorskite group (A. E. Fersman, Bull. Acad. Sci. St. Petersburg, 1908, **2**, 255, 637) the fibres rarely show a parallel arrangement, but are more usually matted and interwoven, giving felted masses known as "mountain-leather," "mountain-cork," and "mountain-wood." It is, however, to be remembered that these trivial names may also be applied to similar aggregates of fibrous amphibole.

From a practical point of view, the most important of these are *tremolite-asbestos* and *serpentine-asbestos*, which in the trade are known as "Italian asbestos" and "Canadian asbestos" respectively. The former is met with as aggregates or bundles of white or greyish fibres, sometimes several feet in length, usually arranged parallel to the surfaces of crevices ("slip-fibre") in the metamorphic and crystalline rocks of mountainous districts. It is mined in the Alps, Urals, and Appalachians. The supply is limited and uncertain, and the hardness of the enclosing rocks makes mining difficult. The principal mines are those in the north of Italy, in the Susa and Aosta valleys in Piedmont, and the Valtellina in Lombardy, and in the Orezza district in Corsica. These are, however, now of little importance, since the use of hornblende-asbestos has been largely replaced by serpentine-asbestos.

Serpentine-asbestos, or chrysotile, occurs in small veins forming an irregular network in serpentine-rock. It has in the closely compacted mass an oil-yellow or greenish colour with a pronounced silky lustre and a certain degree of translucency. When rubbed or crushed, it readily separates into white cottony fibres ("pierre à coton" of the French-Canadians). The fibres are arranged perpendicularly to the walls of the vein ("cross-fibre"), and are usually only an inch or two in length, never exceeding 6 inches. The mineral usually contains 2–3% FeO isomorphously replacing magnesia. Chrysotile is found at all the localities where serpentine-rock occurs (*e.g.* the Lizard district in Cornwall), and it is extensively mined in Canada, Russia, South Africa, and the United States. Of these the most important are the Canadian deposits, which have been worked since 1878. The mining districts are near Thetford Mines, Black Lake, East Broughton and Danville in Quebec; and extend over the United States border into Vermont. The mineral is also mined in Arizona and California. In Russia, the principal deposits are in the Ural Mountains, in the neighbourhood of Ekaterinburg and Orenburg; and there are others in the Caucasus. More recently, rich deposits have been opened up in Southern Rhodesia in the Victoria, Belingwe, and Lomangundi districts, and in the Caroline and Barberton districts in the Transvaal. The asbestos quarried by the ancients at Karystos in Eubœa (Karystian stone), and in Cyprus, was also a serpentine-asbestos (J. W. Evans, Min. Mag. 1906, **14**, 143; Geol. Mag. 1909, **6**, 286). He suggests the name *Karystiolite* as an alternative for chrysotile, owing to its confusion with chrysolite—a synonym of olivine. It was used for wicks in the perpetually burning lamps of the temples; and was woven into napkins, which could be cleansed by fire, and into cremation shrouds.

The blue asbestos or crocidolite (*q.v.*) of South Africa occurs as layers interbedded in the brown jaspers and ironstones of the lower portion of the Pretoria series of sedimentary rocks, and is quarried or mined as slabs in which the fibres of the mineral run perpendicularly or somewhat obliquely to the surfaces. The belt of crocidolite-bearing rocks extends for a distance of about 300 miles with a width of 4–20 miles, from the Orange River through the Asbestos Mountains in Griqualand West into Bechuanaland.

Amosite (so named from the initial letters of the company, Asbestos Mines of South Africa) has been worked in large amounts since 1918 in the Lydenburg and Pietersburg districts in north-eastern Transvaal. In its mode of occurrence as cross-fibre veins in banded jaspery ironstones it is very similar to crocidolite, but it forms longer fibres and is greyish or brownish in colour. It is an anthophyllite-asbestos rich in iron and may be described as ferroanthophyllite. Anthophyllite-asbestos has also been worked in the United States in Georgia and Idaho, and it forms bands of considerable thickness in gneisses and schists in the Morogoro district in Tanganyika Territory.

These various kinds of asbestos differ somewhat in their resistance to acids and heat. Chrysotile is decomposed by hydrochloric and sulphuric acids; at a red heat (but not below) it loses water, and the fibres can be fused in the bunsen-flame. Tremolite-asbestos is not attacked by acids, and it is more difficultly fusible. On the other hand, the fibres of chrysotile are more flexible and more suitable for textile purposes. Crocidolite is readily fusible to a black magnetic glass, but it has the advantage that it is but slightly attacked by acids, chemical solutions, and sea-water. It possesses a greater tensile strength and is more elastic than chrysotile; and is further a good insulator for heat and electricity. Notwithstanding these differences, these varieties of asbestos are put to much the same uses, but serpentine-asbestos is employed in far larger quantities.

Spun asbestos is largely used for steam packings and fireproof curtains; as cloth, twine and rope it finds a variety of applications. As an insulating material, asbestos fibre is used for coating steam and hot-water pipes and cold-storage plants; and as a lining in safes, stoves and furnaces. For use as a constructional fireproof material, it is made into bricks, boards, millboards, plasters, and paints, being often mixed with other materials. The so-called "asbestic," largely used for wall plaster, is prepared by grinding the poorer material and waste, which consists of narrow veins of asbestos still enclosed in the serpentine-rock. In the laboratory, asbestos is used for filtering (a pure white tremolite-asbestos being best for this purpose), for stoppings in combustion tubes, and in the form of card for supports. Asbestos paper or twine, soaked in sodium silicate and afterwards treated with calcium chloride solution, can be used for repairing glass apparatus.

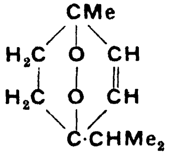
References.—R. H. Jones, "Asbestos" (London, 1890), and "Asbestos and Asbestic" (London, 1897); G. P. Merrill, "Asbestos and other Asbestiform Minerals" (Proc. U.S. Nat. Museum, 1895, **18**, 281), and "Non-metallic Minerals" (New York, 1910); H. Ries, Economic Geology" (New York, 6th ed., 1930); "Asbestos," Imperial Institute (Mineral Resources), London, 1921; W. B. Gamble, "Bibliography of Asbestos" (New York Public Library, 1929).

Canada.—F. Cirkel, "Chrysotile-Asbestos, its occurrence, exploitation, milling, and uses," 2nd ed. (Canada, Mines Branch, 1910, No. 69); J. G. Ross, "Chrysotile Asbestos in Canada" (*ibid.* 1931, No. 707).

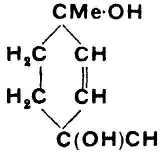
South Africa.—A. L. Hall, "Asbestos in the Union of South Africa" (Mem. Geol. Survey, 1930, No. 12, 2nd ed.) ; M. A. Peacock, "Nature and Origin of the Amphibole-Asbestos of South Africa" (Amer. Min. 1928, **13**, 241) ; F. E. Keep, Bull. Geol. Survey Southern Rhodesia, 1929, **12** ; 1930, **16** ; L. Reinecke and L. McClure, "Amosite Asbestos" (Trans. Geol. Soc. South Africa, 1934, **36**, 29).

India.—A. L. Coulson (Mem. Geol. Survey India, 1934, **64**, 143). L. J. S.

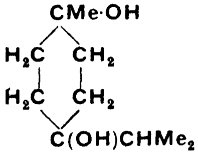
ASCARIDOLE.



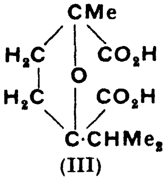
The important anthelmintic, chenopodium or wormseed oil, from *Chenopodium ambrosioides* (var. *anthelminticum*, Gray) has as its pharmacologically active constituent the dioxide, *ascaridole*, b.p. 96°–97°/8 mm., $d^{20°}_{20°}$ 0·9985, $n^{20°}_{D}$ 1·4769, $[\alpha]_D$ +0·7°. Ascaridole was first isolated by Hüthig (Schimmel's Report, 1908, April, p. 108) and its structure was elucidated by the investigations of Nelson (J. Amer. Chem. Soc. 1911, **33**, 1404 ; 1913, **35**, 34) and of Wallach (Annalen, 1912, **392**, 59). The unsaturated peroxide formula has been confirmed by Richter and Presting (Ber. 1931, **64** [B], 878 ; *cf.* Bodendorf, Arch. Pharm. 1933, **271**, 1), who have shown that on partial reduction it yields *p*-Δ^2-*menthene*-1 : 4-*diol* (I), complete reduction giving 1 : 4-*terpin* (II). On oxidation with potassium permanganate it yields 1 : 4-*cineolic acid* (III) and *a-methyl-δ-isopropyl-aδ-dihydroxyadipic acid.* Ascaridole decomposes with explosive violence when heated at 130°–150°, isomerising to *ascaridole glycol anhydride* (IV), b.p. 122°–125°/20 mm., $d^{15°}$ 1·026, $[\alpha]_D$ +0·72°. This isomerisation can be smoothly effected by heating the peroxide in a neutral solvent (xylene) (Henry and Paget, J.C.S. 1921, **119**, 1722). On hydration with sulphuric acid ascaridole glycol anhydride gives two isomeric *glycols* (V), m.p. 62·5°–64° and (VI), m.p. 103°–105°, and an *erythritol* (VII), m.p. 128°–130°. No crystalline derivatives of ascaridole have been prepared. J. L. S.



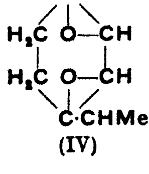
(I)



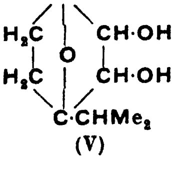
(II)



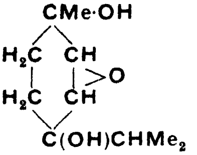
(III)



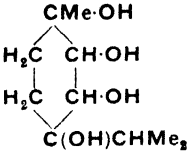
(IV)



(V)



(VI)



(VII)

ASCLEPIAS COTTON. *Vegetable Silk.* The long, lustrous, but brittle fibres, seed hairs, of *A. syriaca* and *A. incarnata* are used for upholstery in the United States, but cannot be spun to a satisfactory thread. The best fibres of *A.* species have been used for cordage in India and South America.

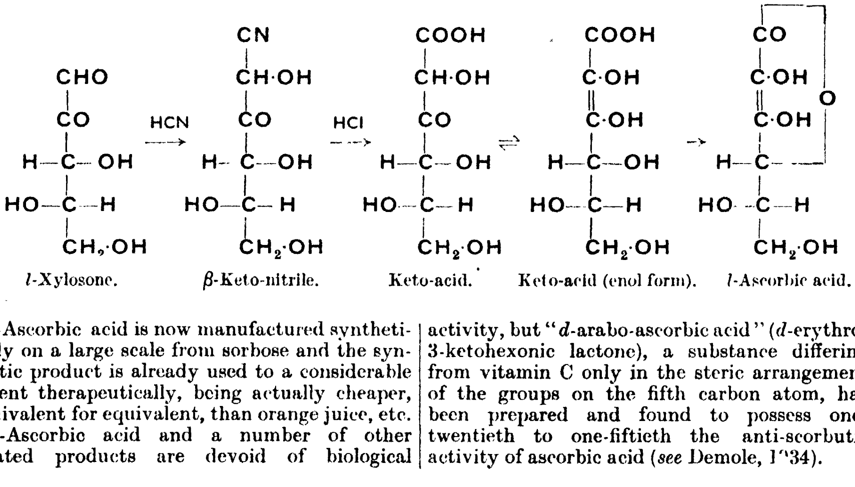
l-ASCORBIC ACID, $C_6H_8O_6$, is vitamin C, or the antiscorbutic vitamin.

Scurvy—vitamin C deficiency—characterised by its typical hæmorrhages, has long been known to arise from the use of diets deficient in fresh foods and to be readily curable by raw fruit, greenstuffs, etc. Early records show that it was common not only among navigators, and in campaigns, but among all the populations of northern latitudes in the winter and spring months. During the nineteenth century the disease was stamped out from the navy and the mercantile marine by the provision of lemon juice. Scurvy is still endemic in isolated regions of the globe, and it has been more widely prevalent than is generally realised ; outbreaks occurred among civilians in all the belligerent countries during the world war (including Great Britain and the U.S.A.), and there were many thousands of cases among troops on all the "fronts." Infantile scurvy (Barlow's disease) has been shown to be associated in a great majority of instances with the use of sterilised or proprietary foods ; supplementary feeding of bottle-fed babies with orange-juice is now a generally accepted routine. It has been inferred that "sub-scurvy," or "incipient scurvy," may be comparatively common, and a certain amount of direct evidence is now available to support the contention.

The proof that scurvy has its origin in a specific vitamin deficiency (and is not due to a bacterial infection, or acidosis, or constipation, or use of tainted food) was furnished by the production of the disease experimentally in guinea-pigs, the first adequate account of which was published by Holst and Frölich in 1907. Experimental scurvy has been described also in the monkey, whereas dogs, rats, fowls, cattle, and probably most other species of animals are able to synthesise their own vitamin and so can dispense with it from the diet.

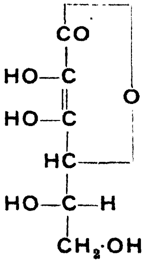
✓ Attempts to isolate vitamin C from lemon juice or orange juice were made by Zilva, whose process depended on precipitation with lead acetate after removal of citric acid and sugar, and by other workers. In 1932 Tillmans and Hirsch noticed that the vitamin C activity of many natural sources went roughly parallel with the presence of a certain reducing principle which they suggested might be identical with the "hexuronic acid" previously isolated by Szent-Györgyi in 1928, from adrenal cortex and cabbage. Shortly afterwards C. G. King and Waugh announced that a crystalline preparation of vitamin C which they had at length succeeded in separating from orange juice had properties resembling hexuronic acid; while Szent-Györgyi and Svirbely tested a specimen of "hexuronic acid" and found it to possess antiscorbutic properties. The suggestion that "hexuronic acid" itself was identical with vitamin C was disputed in some quarters, but Harris and Ray (1932) gave evidence of its specificity by showing that there was in fact an invariable correlation between "hexuronic acid" and antiscorbutic activity. "Hexuronic acid" was renamed ascorbic acid (Szent-Györgyi and Haworth, 1933), and final proof of its identity with vitamin C was furnished by its synthesis. The synthetic product had the same biological activity as the naturally occurring vitamin.

This synthesis of *l*-ascorbic acid, which is the biologically active isomer, was effected almost simultaneously by Reichstein and his co-workers at Zürich and Haworth and Hirst and their co-workers at Birmingham (Ault *et al.*) in 1933, by the reaction shown below, starting from *l*-xylose. The structural formula for ascorbic acid is that finally propounded by the Birmingham workers (Herbert *et al.*, 1933).

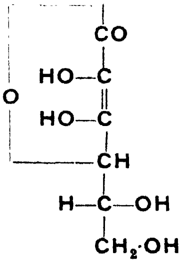


l-Xylosone. *β*-Keto-nitrile. Keto-acid. Keto-acid (enol form). *l*-Ascorbic acid.

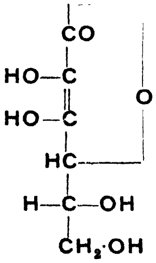
l-Ascorbic acid is now manufactured synthetically on a large scale from sorbose and the synthetic product is already used to a considerable extent therapeutically, being actually cheaper, equivalent for equivalent, than orange juice, etc. *d*-Ascorbic acid and a number of other related products are devoid of biological activity, but "*d*-arabo-ascorbic acid" (*d*-erythro-3-ketohexonic lactone), a substance differing from vitamin C only in the steric arrangement of the groups on the fifth carbon atom, has been prepared and found to possess one-twentieth to one-fiftieth the anti-scorbutic activity of ascorbic acid (*see* Demole, 1934).



l-Ascorbic acid (vitamin C).



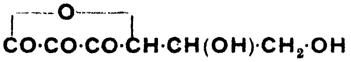
d-Ascorbic acid.



d-Erythro-3-ketohexonic lactone.

Two other closely related substances are now also known to possess antiscorbutic action, *viz.* *l*-rhamno-ascorbic acid (activity=one-fifth) and *l*-gluco-ascorbic acid (activity=one-fortieth) (*see* Reichstein *et al.*, 1935).

Vitamin C is under most conditions very sensitive to heat, alkalinity and oxidation, the latter being apparently the primary factor in its inactivation. The *first* stage in its oxidation, namely, to dehydroascorbic acid, which takes place under certain mild conditions of oxidation, is *reversible*, but under other circumstances oxidation proceeds to the second or irreversible stage:



$$\overbrace{CO\cdot CO\cdot CO\cdot CH}^{O}\cdot CH(OH)\cdot CH_2\cdot OH$$

Dehydroascorbic acid.

The vitamin is soluble in water, ethyl alcohol and methyl alcohol, but not in the usual fat solvents; it is precipitated, *e.g.* from fruit juice, etc., without loss of activity by lead acetate at p_H 7, but not by certain other common precipitating agents ; unlike vitamin B, it is not readily adsorbed on charcoal and fuller's earth, etc.

For the assay of the vitamin in a foodstuff a determination is usually made of the minimum protective dose needed to prevent typical signs of scurvy in guinea-pigs. Another method involves microscopical examination of tooth structure (Höjer). The international unit (League of Nations Health Organisation, 1931) first defined as the " vitamin C activity of 0·1 c.c. of fresh juice of the lemon " is now replaced (1934) by 0·05 mg. of *l*-ascorbic acid. A quantitative titration method (Birch, Harris, and Ray, 1933) based on modifications in the use of Tillmans' indicator (2, 6-dichlorophenolindophenol), a redox indicator of the phenolindophenol type introduced into vitamin C research by Zilva (1927), has recently come into wide use and led to the discovery of vitamin C in a number of hitherto unsuspected sources, *e.g.* eye lens, adrenal medulla, etc. In the gut wall (of the rat) the amount of vitamin C present seems to be linked with the animal's metabolic activities, varying with the balance of the food constituents (Hopkins, 1934). The best known natural sources of the vitamin include lemon, orange, tomato and pineapple juice ; and fresh spinach, cabbage, green peas, and turnips, and green leaves generally. Paprika is particularly rich (Szent-Györgyi, 1932), and so are the "hips" of roses, also blackcurrants. The amount in fresh cows' milk and meat (muscle) is relatively small, but it has recently been shown that liver is a reasonably active source, while the suprarenal cortex definitely exceeds orange or lemon juice (Harris and Ray, 1932). The fact that normal human milk may contain 5–6 times as much as fresh cows' milk (Harris and Ray, 1935) no doubt accounts for the rarity of scurvy in breast-fed infants. There is none of the vitamin in eggs or in yeast. Many canning and drying processes and ageing may entail a considerable loss of antiscorbutic activity, but canned blackcurrants or tomatoes, for example, may be highly potent. Numerous unsuccessful efforts have been made to find a chemical preservative for the vitamin ; recent observations suggest that aeration of fruit juice with CO_2 may serve the purpose (*see* Morgan *et al.*, 1933). The presence of copper especially catalyzes the oxidation, *e.g.* as in commercial pasteurisation machinery for milk.

Vitamin C is synthesised during the germination of seeds (Fürst, 1912), but contrary to earlier clinical theories ultra-violet light is not necessary for this synthesis, nor has it any curative or protective action on scorbutic animals. The vitamin is excreted in the urine in amounts varying on the quantity present in the food, and the urinary " response " is used as a test for vitamin C subnutrition (Harris *et al.*, 1933, 1936). More vitamin C is metabolised in the body, and less is excreted in the urine, in various infectious diseases—which therefore seem to increase the need for this factor.

The physiological action of vitamin C is presumably due largely to its peculiar reducing activity, associated in some way with the characteristic " endiol " group,

$$-(HO)C{=}C(OH)-$$

The distinctive histological changes in vitamin C deficiency in bone and teeth, can be traced primarily to the need of certain specialised cells, such as osteoblasts, odontoblasts, ameloblasts, etc., for vitamin C to enable them to continue their normal functional activities, other effects being secondary (Fish and Harris, 1934).

The minimal-optimum daily dose of vitamin C for an adult human being appears to be about 25 mg., and a child needs quite twice as much on a body-weight basis. L. J. H.

ASDUANA *v.* BRIDELIA BARK.

ASEPTOL. Trade name for phenol-4 sulphonic acid. Antiseptic.

ASH. The composition of the ash, which remains after an organic substance is burnt, varies both qualitatively and quantitatively according to the method of incineration employed. For convenience, all the mineral constituents of living things will be considered under this heading ; but a number of them do not remain in the ash unless special methods of ashing are employed. It has long been realised that when ordinary methods of incineration are employed chlorine and sulphur may be partially or completely lost, phosphates tend to be reduced by the hot carbon and there is a variable loss of alkali metals by volatilisation. Berthelot mixed the substance with a known weight of sodium carbonate and heated in a stream of oxygen in an attempt to overcome these difficulties (Compt. rend. 1899, **128**, 23). Since then numerous other methods have been tried ; perhaps the most generally adopted method for preventing loss of alkali chlorides is first to char the material thoroughly at a moderate temperature, extract the cooled residue, then dry and ignite the residue at a higher temperature until all carbon is oxidised ; finally the aqueous extract is added, evaporated to dryness and the residue is heated gently. Ammonium nitrate is sometimes added to the black char to hasten the oxidation of the carbon. Even when this method is adopted appreciable quantities of both sulphur and chlorine may be lost. When accurate determinations of these two elements are desired they should be carried out on aliquot portions of the organic material. Magnesium nitrate may be added to prevent loss of sulphur and sodium carbonate to prevent loss of chlorine.

In 1870 Liebig (" Chemistry in its Application to Agriculture and Physiology ") contended that, since plants derive their carbon from the carbon dioxide of the atmosphere, all that is necessary to preserve the fertility of the soil is to return to it in a suitable form the mineral constituents and nitrogen removed from it by the crop. For some decades after this much work was done on the ash analysis of plants. Many of the results obtained were collected together by E. Wolff (" Aschen-analysen von landwirtschaftlichen Producten, Fabrikabfällen and wildwachsenden Pflanzen," Berlin, 1871) (*see* Table, pp. 508–9). These and later results have shown that the mineral analysis of a crop is not a reliable index of its manurial requirements. Thus Lawes at Rothamsted showed that, though turnips usually contain relatively little phosphorus, yet they responded markedly to applications of phosphates to the soil.

Not only do different species of plants, growing in the same soil, but even varieties of the same species growing under the same conditions, vary in mineral composition. Some plants, for example fruit trees, are commonly budded or grafted on root systems of another variety, or even species; the mineral composition of the scion, or top part, is then influenced markedly by the rootstock (J. W. Brown, Ann. Bot. 1926, **40**, 129; W. A. Roach, Nature, 1933, **131**, 202; F. M. Eaton, G. Y. Blair, Plant Physiology, 1935, **10**, 411).

The mineral composition of a given sort of plant varies also from soil to soil and is influenced by the manure applied to the soil and by the climatic conditions.

The interpretation of the results of ash analysis, therefore, presents problems of great complexity. The earlier work was concerned mainly with the metals, potassium, calcium, magnesium, sodium; and the non-metals, phosphorus, silicon, sulphur, and chlorine, all of which occur in relatively large amounts; but some attention was paid to elements occurring in small amount, and the fact that iron, even though occurring in minute amount, was essential for the growth of green plants, was realised.

Of late years increasing attention has been, and is still being, paid to a number of elements which occur in minute amount only, but are either essential for health to animals or plants or both, or have important accessory functions. Some of these elements, as will be seen later, are only required in infinitesimal quantities.

The essential nature of the elements occurring in comparatively large amount was readily demonstrated by growing plants in water culture, *i.e.* in dilute solutions containing salts of the elements. For a long time the importance of the "trace" elements was not suspected because the purest salts used for water culture experiments contained enough of all of these elements to supply the needs of the plants, and even now when such experiments are carried out all chemicals have to be purified specially for the end in view; and the receptacle for the culture solutions must be chosen with great care since experiments have been vitiated through substances in the walls of the vessel (*e.g.* boron from the glaze on earthenware) passing into the solution in sufficient quantity to supply the needs of the plants, or even in sufficient quantity to inhibit growth (*e.g.* boron may pass into solution from the walls of vessels of certain types of glass in sufficient quantity to prevent growth of micro-organisms grown in them).

Injection of mineral salts into plants, especially trees, is being used as a method of studying the functions of elements in plant nutrition. Examples are given later under boron, copper, iron, etc. Recent analytical work has reflected more and more the interest in the trace elements. Many spectroscopic methods have been developed for this work (H. Ramage, Nature, 1929, **123**, 601). The polarographic method (Heyrovsky, Microchemie, 1932, **12**, 25) promises to be of great value, and various microchemical methods have also been applied with success.

The results of chemical analysis must be interpreted with great caution; the mere presence of an element in a plant or animal does not prove that it is physiologically active; an essential element such as iron may be present in a plant in normal amount but, because it is in the wrong form (*e.g.* insoluble phosphate), the plant may become *chlorotic*, showing that the iron is not functioning properly; further, plants absorb not only the elements necessary for healthy growth but others which may be in the solution bathing their roots and which, as far as is known, do not affect metabolism adversely unless they are in excessive amounts. A further difficulty in interpreting the results of chemical analysis is occasioned by the large number of elements often present; thus apple trees contain over twenty elements (W. A. Roach, Annual Report East Malling Research Station for 1928–1930, 1931, 101).

Most striking results have been obtained by applying salts of "trace" elements to the soil; for example, R. S. Young has reported increased growth of timothy grass and oats resulting from the application of each of thirty-three different trace elements to soil (Cornell, Univ. Agric. Expt. Sta. 1935, Memoir 174), but such results are difficult to interpret because many of these elements are readily absorbed by the solid soil particles, equivalent amounts of other elements being liberated into solution in their stead. The elements which occur in plants and animals will now be given in alphabetical order with some indication of our knowledge of what functions, if any, they serve.

Aluminium.—G. Bertrand and G. Lévy (Compt. rend. Acad. Agric. France, 1931, **17**, 235) detected aluminium in all the phanerograms tested, in amounts varying from 0·5 to 1,460 mg. per kg. Grains were proved to be relatively poor and leaves rich in the element. Hence man and animals often consume more aluminium than iron in green foodstuffs.

P. Mazé (Ann. Inst. Pasteur, 1914, **28**, 21; 1919, **33**, 139) concluded from the results of water culture experiments that aluminium is essential for the growth of maize. Anna L. Sommer (Univ. California Publ. Agric. Sci. 1926, **5**, 2, 57), also using water culture methods, obtained an increase in dry weight with peas and a large increase in growth, and more so in seed production, in millet, as a result of the addition of 1 p.p.m. of aluminium as $Al_2(SO_4)_3$.

The Mellon Institute of Industrial Research has published a select, annotated bibliography on the hygienic aspects of aluminium and aluminium utensils (Bibliographic series, 1933, Bul. 3), and a similar report entitled "Aluminium in Food," by G. W. Monier Williams, has been published by the Ministry of Health (Reports on Public Health and Medical Subjects, No. 78, 1935). There is, however, still no definite evidence for or and against the deleterious action of aluminium when this metal is used for cooking utensils, and the question must therefore be regarded as *sub judice.*

Arsenic.—Jadin and Astruc (Compt. rend. 1914, **159**, 268) detected arsenic in minute quantities in a wide range of plants ; but it is not known whether it plays any important part in the plant's metabolism.

Barium.—McHargue (J. Amer. Chem. Soc. 1913, **35**, 826 ; J. Agric. Res. 1919, **16**, 183) reported the wide occurrence of barium in plants; this element in the absence of lime is poisonous, but in the presence of excess lime is stimulating.

Boron.—This element occurs to the extent of a fraction of 0·1% in the ash of most, if not all, plants (W. E. Brenchley, " Inorganic Plant Poisons and Stimulants," Cambridge, 1927), and evidence has accumulated rapidly that boron is essential for the growth of plants. W. E. Brenchley and K. Warrington (Ann. Bot. 1927, **161**, 167), working on broad beans, showed that boron could not be replaced by any of the fifty-two elements tested.

A. L. Sommer and C. B. Lipman (Plant Physiol. 1926, **1**, 231) proved boron to be essential to sunflowers, cotton, barley, buckwheat, castor beans, flax, and mustard. They describe in detail the refined methods necessary for proving the essential nature of a trace element such as boron.

Different species of plants vary in their needs for boron, and in the extent to which they absorb it. F. M. Eaton, G. Y. Blair (Plant Physiol. 1935, **10**, 411), C. S. Scofield, and L. V. Wilcox (U.S. Agric. Dept. 1931 Tech. Bull. 264) stated that plants varied in their resistance to damage to excessive concentrations ; that a boron content of more than 0·5 p.p.m. in irrigation waters was injurious to sensitive plants such as lemon and walnut, and that cereals, cotton, and alfalfa were more resistant.

W. E. Brenchley and H. G. Thornton (Proc. Roy. Soc. 1925, B, **98**, 373) proved that the presence of boron was essential for the normal growth and functioning of nodules on the broad bean. K. Warington (Ann. Bot. 1926, **157**, 27) described deep-seated abnormalities of anatomical structure in broad beans grown in the absence of boron.

Certain physiological diseases of plants may be cured by treatment with boron compounds, and as far as is known by no other means. An example is mottle leaf in citrus. A. R. C. Haas (Hilgardia, 1932, **6**, 483), A. R. C. Haas and J. Klotz (*ibid.* 1931, **5**, 175 ; Bot. Gaz. 1931, **92**, 94) showed that boron was essential for cambium activity.

E. Brandenburg (Phytopath. Z. 1931, **3**, 499 ; Angew. Bot. 1932, **14**, 194), showed that heart rot in beet was caused by a deficiency of boron and could be cured by additions of boric acid or borax.

J. D. Atkinson (New Zealand J. Sci. Tech. 1935, **16**, 316) cured three apple trees, the fruit of which was affected by corky core, by injecting them with solutions containing 4, 5, and 8 g. of boric acid respectively. H. O. Askew (New Zealand J. Sci. Tech. 1935, **17**, 388), as a result of analysing leaves and fruit from healthy and affected trees, found that the boron content was inversely proportional to the degree of severity of the ailment. The boron content varied from 3 to 8 p.p.m. on dry matter for affected apples and from 10 to 13 p.p.m. for healthy fruit ; the corresponding figures for leaves were 9 to 11 and 17 to 18 respectively.

Recently H. R. McLarty has cured apple trees suffering from drought spot and corky core by injecting into their stems solutions of boric acid or a borate ; more boron was necessary to cure the corky core than the drought spot. The crop was increased about sevenfold. (Private communication.)

Bromine.—A. Damiens and S. Blaignan (Compt. rend. 1931, **193**, 1460 ; 1932, **194**, 2077) detected bromine in a large number of plants ; the quantity varied up to 2 mg. per 100 g. of dry matter ; it was not detected in rice or beans.

Cæsium.—Was detected by Bertrand in sugar beet (Ann. Inst. Pasteur, 1912, **26**, 852) and by Robinson, Steinkoenig and Miller in other plants (U.S. Dept. Agric. Bull. No. 600 (1917)), Nakamura (Bull. Agric. Coll. Tokyo, **6**, 1904) and Loew (Chem.-Ztg. 1913, **37**, 61) reported that cæsium salts in small quantities had a stimulating action on plants.

Calcium is one of the elements occurring in greatest abundance in plant ash, of which lime commonly makes up 10–50%. It occurs in all parts of plants and, as calcium pectate is the main constituent of the middle lamella. It occurs in certain plants as calcium oxalate crystals. Lime is also abundant in the ash of animal carcases, of which it makes up about 30%. Calcium phosphate is the main mineral constituent of the bony skeleton of animals.

Chlorine.—Jung (Sitzungsber. Akad. Wiss. Wien, 1920, **129**, 297) detected chlorine in nearly all the plants tested, except conifers. Mazé (Ann. Inst. Pasteur, 1914, **28**, 21) reported that chlorine was essential to maize.

Chromium.—Robinson, Steinkoenig, and Miller (U.S. Dept. Agric. Bull. No. 600 (1917)) detected chromium in many plants. Koenig (Chem.-Ztg. 1911, **35**, 442) reported dilute solutions of chromous salts to be stimulating to plants.

Cobalt.—E. R. Bishop and M. Lawrence (Science, 1932, **75**, 264) detected cobalt in all plants giving green or blue ashes. Bertrand and Makragnatz (Compt. rend. 1922, **175**, 458 ; Bull. Soc. chim. 1925, **37**, 554 ; *ibid.* 1930, **47**, 326) detected cobalt in all vegetables and cereals (except carrots and oats) and in many other plants.

Low concentrations of cobalt salts were found to be stimulating to maize and barley by K. Scharrer and W. Schropp (Biochem. Z. 1931, **236**, 187).

Cobalt is commonly, if not always, present in minute traces in animal bodies. Bertrand and Mancheboeuf (Compt. rend. 1925, **180**, 1380 ; *ibid.* 1993 ; Bull. Soc. chim. 1925, **37**, 934). The pancreas is one of the organs richest in cobalt (Bertrand and Mancheboeuf, Bull. Soc. chim. 1926, **39**, 1646 ; *see also* Fox and Ramage, Proc. Roy. Soc. 1931, **108B**, 157).

Recently the administration of 1 mg. per day of cobalt, as cobaltous nitrate, to sheep suffering from "coast disease," which is usually fatal, has led to a rapid and complete cure (E. W. Lines, J. Council for Sci. Ind. Res. Australia, 1935, **8**, 117).

Copper.—Some measure of the attention paid to copper in recent years is given by the fact that 177 references to it are given in the "Bibliography of the more important heavy metals occurring in food and biological material," 1921–1933, 30 pp., compiled for the Society of Public Analysts, 1934.

It is of nearly, or quite, universal occurrence in plants in minute amounts ; and the results of most recent investigations suggest that it is an essential element ; for example, A. L. Sommer (American Fertilizer, 1930, **72**, 15 ; Plant Physiol. 1931, **6**, 339) found copper essential for the normal growth of sunflowers and tomatoes, and C. B. Lipman and G. Mackinney (*ibid.* 593) showed that barley was unable to produce seeds in the absence of copper.

The exanthema disease of citrus and other fruits has been shown to be due to a shortage of copper and to be cured by application of copper compounds to the soil, by spraying of Bordeaux mixture on the foliage (A. R. C. Haas and H. J. Quayle, Hilgardia, 1935, **9**, 143), or by injection of solutions of copper compounds into the trees (H. E. Thomas, Phytopath. 1931, **21**, 995).

Copper is of wide occurrence in the animal kingdom. It occurs in blood serum, J. Waddell, H. Steenbock, and E. B. Hart (J. Biol. Chem. 1929, **84**, 115), and F. A. Underhill, J. M. Orten, and R. C. Lewis (J. Biol. Chem. 1931, **91**, 13) used copper to supplement iron in curing nutritional anæmia in rats and stated that no other metals could replace copper in this respect. The work of V. C. Myers and H. H. Beard, however, has not supported this conclusion (J. Biol. Chem. 1931, **94**, 89).

McHargue (Amer. J. Physiol. 1926, **77**, 240) found that the growth of rats was improved when small quantities of copper salts were included in their food. Hart and Steenbock (J. Biol. Chem. 1928, **77**, 797) state that copper is essential in nutrition to permit of the assimilation of iron to form hæmoglobin.

It has long been known that the blood of certain of the lower animals (*e.g.* some crustaceans, cuttle-fish, snails) contains, instead of the red hæmoglobin, a green or blue colouring substance—hæmocyanin—which contains copper instead of iron. Redfield, Coolidge, and Shotts (J. Biol. Chem. 1928, **76**, 185) found that hæmocyanin from the blood of *Limulus polyphemus* contains 0·173% of copper.

Blood of the usual red colour, due to hæmoglobin, has been shown to contain copper in the serum. Warburg and Klebs (Biochem. Z. 1927, **187**, 143) found in the serum of human blood $1{\cdot}7\times10^{-3}$ mg. of loosely combined copper per c.c., and only about $0{\cdot}7\times10^{-3}$ mg. of loosely combined iron. Schonheimer and Oshima (Z. physiol. Chem. 1929, **180**, 240) found copper in the blood of a large number of animals, the proportion being about 1·0–1·5 mg. per kg.

Fluorine.—This element has been found in many plants. It tends to accumulate most in the leaves (A. Gautier and P. Clausmann, Compt. rend. 1916, **162**, 105). P. Mazé found fluorine to be essential for the growth of maize in water culture (Ann. Inst. Pasteur, 1914, **28**, 21 ; 1919, **33**, 139) and A. Gautier and P. Clausmann reported increased yields of wheat, oats, carrots, potatoes, peas, poppies, and beans as a result of applications of calcium fluoride. W. H. Sebrell, H. T. Dean, E. Elvove, and R. P. Breaux found an association of the incidence of mottled teeth in man and animals with the presence of fluorine in drinking water (U.S. Pub. Health Serv., Public Health Reports, 1933, **48**, 437).

Iodine.—This element was found essential for the growth of maize in water culture by P. Mazé (Ann. Inst. Pasteur, 1914, **28**, 21 ; 1919, **33**, 139). Beneficial effects of the addition of this element to water culture and to soil have also been recorded by J. Stocklasa (Biochem. Z. 1926, **176**, 38 ; Protoplasma, 1929, **8**, 199 ; Z. Ernähr. 1931, **1**, 3) and by O. Loew (Z. Pflanz. Düng. 1926, A, **7**, 233).

That the thyroid gland in man and in many animals contains iodine was discovered by Baumann in 1895, and in 1915 Kendall (J. Amer. Med. Assoc. 1915, **64**, 2042) isolated *thyroxin*, the essential secretion of the gland.

A suitable secretion of thyroxin in an animal is apparently essential for normal metabolism. The average proportion of iodine in the thyroid gland is about 2 mg. per gram, with a total of about 40 mg. of iodine in the whole adult human thyroid.

It has been proved that a lack of iodine in the diet often leads to an enlargement of the thyroid gland and the disease known as goitre or cretinism. The prevalence of this disease is correlated with the paucity of iodine in the soil and drinking water of various districts, and one important factor seems to be the distance from the sea.

Reith (Rec. trav. chim. 1930, **49**, 142) found that the amount of iodine in sea-water from various localities and from different depths varied only slightly—from 43 to 69 mg. per litre.

In places far inland the waters of the rivers and lakes are often almost devoid of iodine. McClendon (J. Amer. Med. Assoc. 1924, **82**, 1668) estimated that the water of Lake Superior contains about 1 part of iodine in 100,000,000,000 parts of water, while that of the lower Mississippi contains from 10,000 to 15,000 times as much.

Plants are able to extract from water a portion of the iodine but, with the exception of certain seaweeds, plants as a rule contain very little of this element. Pfeiffer and Courth (Biochem. Z. 1929, **213**, 74) found that carrots and radishes were able to store up iodine in the form of organic compounds.

T. von Fellenberg (Biochem. Z. 1923, **142**, 246) estimated that a human adult requires about 0·0014 g. of iodine daily, and that a reserve store can be built up in the body if the food consumed can supply it.

"Iodised" salt now frequently replaces "rock salt" for the use of stabled or stall-fed animals.

Iron.—Iron occurs in minute amount in all green plants and is essential for their growth. Though not a constituent of chlorophyll, iron appears to be essential for its formation. Plants grown in the absence of iron are cream-coloured instead of green. This chlorotic appearance disappears if the plant is treated with a suitable iron compound and it takes on its normal green colour, this change may be effected by applying soluble iron salts to the soil, but often such treatment is useless since the iron is precipitated either in the soil or, after absorption, by the plant. Olsen has shown that in water culture chlorosis occurs in the presence of iron, only when the hydrogen ion concentration is within certain limits (p_H 6–7), and then only in the absence of humus ; but excess of phosphate increases the tendency to chlorosis as a result of the iron being precipitated as iron phosphate (Compt. rend. Trav. Lab. Carlsberg, 1935, **21**, 15).

Chlorotic plants often contain more iron than normal green ones, the iron being in some form, probably phosphate, unavailable to the plant. Iron in salts of organic acids is not so easily precipitated as phosphate. Consequently the trace of iron included in culture solutions is now usually added in the form of ferric citrate instead of the ferric chloride used by older workers.

Chlorotic plants, such as apple trees, may sometimes, but not always, be cured by growing a green crop such as grass below them (T. Wallace, J. Pomology and Horticultural Science, 1929, **7**, 251). As far as is known plants suffering from chlorosis of the iron shortage type can always be cured, either by treating the foliage with solutions of iron salts or by injecting iron salts either in solution (J. Sachs, Naturw. Rundschau. 1886, **1**, 257) or in solid form. According to J. P. Bennett (Univ. California, Coll. Agric. 1931, Circular 321) this solid salt method is now applied commercially on a large scale in America.

Iron is contained in the hæmoglobin molecule and is thus an essential element for all animals with red blood (*see also* copper).

Lead.—Lead occurs fairly widely in plants. R. Berg recorded 1 mg. per 100 g. of cereals (Biochem. Z. 1925, **165**, 461). Increases of yield have often been recorded as a result of application of lead salts to the soil, but there is no definite evidence that this was the direct result of lead on the plants rather than an indirect one due to the liberation into solution of some other element in the soil particles by the lead.

J. J. Griffith reported lead to be localised in regions of growth by cell division (J. Agric. Sci. 1919, **9**, 366). W. A. Roach reported lead to be present in the root wood of certain apple trees but to be absent from the root bark and all other parts of the tree (Ann. Rep. East Malling Research Station for 1929–1930, 1931, 101).

Traces of lead occur sporadically in different organs of the human body (J. H. Sheldon and H. Ramage, Biochem. J. 1931, **25**, 1608 ; S. L. Tompsett, A. B. Anderson, Biochem. J. 1935, **39**, 1851) ; and the metal is a normal constituent of animal tissue (G. Bertrand and Cinrea, Compt. rend. 1931, **192**, 990).

Lead, in more than traces, is harmful to plants (Griffith, *l.c.*), animals and man.

Lithium.—Lithium is widely distributed in plants (W. O. Robinson, L. A. Steinkoenig, C. F. Miller (U.S. Agric. Dept. (1917) Bull. 600).

Magnesium.—Magnesium, being a constituent of chlorophyll, is therefore an essential element in green plants. Some plants contain as much magnesium as calcium though this is unusual. E. Canals (Bull. Soc. Chim. biol. 1929, **11**, 14) concluded that the invertase molecule contains magnesium in non-ionic form.

C. B. Lipman and A. Gordon (J. Gen. Physiol. 1925, **7**, 615) reported that the injection of magnesium salts in solution into fruit trees resulted in a striking improvement in the foliage. In Technical Communication No. 31, 1934, of the Imperial Bureau of Soil Science, entitled " Soil Deficiencies and Plant Diseases," many instances are given of plants benefiting from the application of magnesium salts to the soil.

Manganese.—The presence of manganese in plants was known at least as early as 1804 (De Saussure, " Recherches sur la végétation," Paris, 1804). Numerous analyses show that the ashes of different plants vary widely in Mn_3O_4 content ; beech leaf ash may contain 11%, that of birch 1%, or less, which is a more usual figure. For a review of the extensive literature, *see* W. E. Brenchley, " Inorganic Plant Poisons and Stimulants," Cambridge, 1927, and R. S. Young (Cornell Univ. Agric. Exp. Sta. Mem. 1935, No. **174**, 70 pp.). G. Samuel and C. S. Piper (Annals of Applied Biology, 1929, **16**, 493) proved by water-culture experiments that manganese is an essential element for oats, peas, beans, clovers, wheat, barley, maize, grasses, and tomatoes.

Diseases due to manganese deficiency have been recorded all over the world. The best known of these is the " grey speck " disease of oats. These deficiencies may be remedied by applications of manganese salts to the soil (Technical Communication No. 31, Imperial Bureau of Soil Science, 1934).

Molybdenum.—The presence of traces of molybdenum in the below-ground woody parts of certain apple trees has been reported by W. A. Roach (Annual Report East Malling Research Station, 1931, 101), in *Azolla*, an aquatic plant, by ter Meulen (Nature, 1932, **130**, 966), and in the leaves of a number of trees by ter Meulen and H. J. Ravenswaay (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 7), who concluded from this, and from the fact that the most fertile soils are richest in molybdenum, that this element must be considered an essential constituent of plants.

Increased growth of *Azotobacter chroococcum* resulting from the application of molybdenum compounds to the culture solutions has been reported by H. Bortels (Arch. Mikrobiol. 1930, **1**, 333), D. Burk and H. Lineweaver (*ibid.* 1931, **2**, 155) ; and L. Birch-Hirschfeld (*ibid.* 1932, **3**, 341) has reported an increase in nitrogen fixation of 150% as a result of the addition of 0·005% Na_2MoO_4 to the culture solution.

The following table, compiled chiefly from Wolff's analyses, gives the average proportions of ash and of its chief components in various fresh or air-dried agricultural products.

100 parts of the substance contain :

Substance.	Water.	Ash.	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
I. *Green Fodder.*											
Meadow grass	70·0	2·33	0·60	0·16	0·11	0·27	0·15	0·12	0·69	0·19	0·06
Rye grass	70·0	2·13	0·53	0·09	0·05	0·16	0·17	0·08	0·84	0·11	0·07
Timothy grass	70·0	2·10	0·61	0·06	0·08	0·20	0·23	0·08	0·75	0·11	0·08
Oats, in blossom	77·0	1·66	0·65	0·06	0·05	0·11	0·14	0·05	0·55	0·07	0·04
Barley, ,,	68·0	2·25	0·59	0·01	0·07	0·14	0·22	0·07	1·08	0·08	0·07
Wheat, ,,	69·0	2·17	0·56	0·01	0·05	0·07	0·16	0·04	1·23	0·06	0·05
Rye fodder	70·0	1·63	0·63	0·01	0·05	0·12	0·24	0·02	0·52	—	—
Red clover	80·0	1·34	0·46	0·02	0·16	0·46	0·13	0·04	0·04	0·05	0·05
White clover	81·0	1·36	0·24	0·11	0·14	0·44	0·20	0·12	0·06	0·04	0·06
Lucerne	75·3	1·76	0·45	0·02	0·10	0·85	0·15	0·11	0·04	0·03	0·08
Sainfoin	78·5	1·16	0·46	0·02	0·07	0·37	0·12	0·04	0·05	0·03	—
Green vetches	82·0	1·57	0·66	0·05	0·11	0·41	0·20	0·06	0·03	0·05	0·03
Potato tops	77·0	1·18	0·07	0·01	0·27	0·55	0·06	0·06	0·05	0·04	0·05
Mangold tops	90·7	1·48	0·43	0·31	0·14	0·17	0·08	0·11	0·07	0·17	0·05
Sugar-beet tops	89·7	1·80	0·40	0·30	0·33	0·36	0·13	0·14	0·06	0·10	—
Turnip tops	89·8	1·40	0·32	0·11	0·06	0·45	0·13	0·14	0·05	0·12	0·05
Chicory tops	85·0	1·87	1·12	0·01	0·06	0·27	0·17	0·17	0·02	0·03	—
Carrot tops	80·8	2·61	0·37	0·60	0·12	0·86	0·12	0·21	0·15	0·19	0·14
Cabbage heads	88·5	1·24	0·60	0·05	0·04	0·19	0·20	0·11	0·01	0·03	0·05
Kohl-rabi tops	85·0	2·53	0·36	0·10	0·10	0·84	0·26	0·30	0·26	0·10	—
II. *Hay and Straw.*											
Meadow hay	14·4	6·66	1·71	0·47	0·33	0·77	0·41	0·34	1·97	0·53	0·17
Red clover hay	16·0	5·65	1·95	0·09	0·69	1·92	0·56	0·17	0·15	0·21	0·21
White clover hay	16·0	6·03	1·06	0·47	0·60	1·94	0·85	0·53	0·27	0·19	0·27
Lucerne hay	16·0	6·00	1·52	0·07	0·35	2·88	0·51	0·37	0·12	0·11	0·26
Sainfoin hay	16·0	4·53	1·79	0·08	0·26	1·46	0·47	0·15	0·18	0·14	—
Oat hay	14·5	6·18	2·41	0·20	0·20	0·41	0·51	0·17	2·05	0·25	0·15
Wheat straw	14·1	4·26	0·49	0·12	0·11	0·26	0·23	0·12	2·82	—	0·16
Rye straw	15·4	4·07	0·76	0·13	0·13	0·31	0·19	0·08	2·37	—	0·09
Barley straw	14·0	4·39	0·93	0·20	0·11	0·33	0·19	0·16	2·36	—	0·13
Oat straw	14·1	4·40	0·97	0·23	0·18	0·36	0·18	0·15	2·11	—	0·17
Maize straw	14·0	4·72	1·66	0·05	0·26	0·50	0·38	0·25	1·79	—	0·39
Pea straw	14·3	4·92	1·07	0·26	0·38	1·86	0·38	0·28	0·28	0·30	0·07
Field bean straw	18·0	5·84	2·59	0·22	0·46	1·35	0·41	0·01	0·31	0·81	0·22
Buckwheat straw	16·0	5·17	2·41	0·11	0·19	0·95	0·61	0·27	0·28	0·40	—
Flax straw	14·0	3·19	1·18	0·16	0·23	0·83	0·43	0·20	0·22	0·15	0·14
Flax, whole plant	25·0	3·23	1·13	0·15	0·29	0·50	0·74	0·16	0·08	0·19	—
Hop, ,, ,,	25·0	7·40	1·94	0·28	0·43	1·18	0·90	0·38	1·59	0·34	0·20
Hops	12·0	5·98	2·23	0·13	0·21	1·01	0·90	0·16	0·92	0·02	0·48
Tobacco	18·0	19·75	5·41	0·73	2·07	7·31	0·71	0·77	1·92	0·88	—
Heather	20·0	3·61	0·48	0·19	0·30	0·68	0·18	0·16	1·27	0·08	—
Broom	16·0	4·89	0·69	0·05	0·28	0·32	0·16	0·07	0·19	0·05	—
Fern	16·0	5·89	2·52	0·27	0·45	0·83	0·57	0·30	0·36	0·60	—
Reeds	18·0	3·85	0·33	0·01	0·05	0·23	0·08	0·11	2·75	—	—
Sedge	14·0	6·95	2·31	0·51	0·29	0·37	0·47	0·23	2·18	0·39	—
Rush	14·0	4·56	1·67	0·30	0·29	0·43	0·29	0·40	0·50	0·65	—
III. *Root Crops.*											
Potato	75·0	0·94	0·56	0·01	0·04	0·02	0·18	0·06	0·02	0·03	0·02
Artichoke	80·0	1·03	0·67	—	0·03	0·04	0·16	0·03	—	0·02	—
Mangold	88·3	0·80	0·43	0·12	0·04	0·04	0·08	0·03	0·02	0·05	0·02
Sugar beet	81·6	0·80	0·40	0·08	0·07	0·05	0·11	0·04	0·03	0·02	—
Turnip	90·9	0·75	0·30	0·08	0·03	0·08	0·10	0·11	0·02	0·03	0·04
White turnip	91·5	0·61	0·31	0·02	0·02	0·08	0·11	0·04	0·01	0·04	—
Kohl-rabi	87·7	0·95	0·49	0·06	0·02	0·09	0·14	0·08	0·01	0·05	—
Carrot	86·0	0·88	0·32	0·19	0·05	0·09	0·11	0·06	0·02	0·03	0·01
Chicory	80·0	1·04	0·42	0·08	0·07	0·09	0·15	0·10	0·06	0·04	—

Substance.	Water.	Ash.	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
IV. *Grains and Seeds.*											
Wheat	14·3	1·77	0·55	0·06	0·22	0·06	0·82	0·04	0·03	—	0·15
Rye	14·9	1·73	0·54	0·03	0·19	0·05	0·82	0·04	0·03	—	0·17
Barley	14·5	2·18	0·48	0·06	0·18	0·05	0·72	0·05	0·59	—	0·14
Oats	14·0	2·64	0·42	0·10	0·18	0·10	0·55	0·04	1·23	—	0·17
Spelt	14·8	3·58	0·62	0·06	0·21	0·09	0·72	0·06	1·58	—	—
Maize	13·6	1·23	0·33	0·02	0·18	0·03	0·55	0·01	0·03	—	0·12
Sorghum	14·0	1·60	0·42	0·05	0·24	0·02	0·81	—	0·12	—	—
Millet	13·0	3·90	0·47	0·04	0·33	0·04	0·91	0·01	2·05	—	0·18
Paddy rice	12·0	6·90	1·27	0·31	0·59	0·35	3·26	0·04	0·04	—	—
Rice	13·0	0·34	0·08	0·02	0·05	0·01	0·17	—	0·01	—	—
Buckwheat	14·1	0·92	0·21	0·06	0·12	0·03	0·44	0·02	—	0·02	—
Flax seed	11·8	3·22	1·04	0·06	0·42	0·27	1·30	0·04	0·04	—	0·17
Peas	13·8	2·42	0·98	0·09	0·19	0·12	0·88	0·08	0·02	0·06	0·24
Field beans	14·1	2·96	1·20	0·04	0·20	0·15	1·16	0·15	0·04	0·08	0·23
V. *Fruits, etc.*											
Apple, whole fruit	84·0	0·27	0·10	0·07	0·02	0·01	0·04	0·02	0·01	—	—
Pear, ,, ,,	80·0	0·41	0·22	0·04	0·02	0·03	0·06	0·02	0·01	—	—
Cherry, ,, ,,	78·0	0·43	0·22	0·01	0·02	0·03	0·07	0·02	0·04	0·01	—
Plum, ,, ,,	82·0	0·40	0·24	—	0·02	0·04	0·06	0·02	0·01	—	—
Acorns, fresh	56·0	0·96	0·62	0·01	0·05	0·07	0·16	0·05	0·02	0·01	—
Beech mast	18·0	2·71	0·62	0·27	0·31	0·67	0·56	0·06	0·05	0·01	—
Horse chestnuts	49·2	1·20	0·71	—	0·01	0·14	0·27	0·02	—	0·08	—
VI. *Leaves—Autumn.*											
Mulberry	67·0	1·17	0·23	—	0·06	0·30	0·12	0·01	0·41	—	—
Horse chestnut	60·0	3·01	0·59	—	0·24	1·22	0·25	0·05	0·42	0·12	—
Walnut	60·0	2·84	0·76	—	0·28	1·53	0·11	0·08	0·06	0·02	—
Beech	55·0	3·05	0·16	0·02	0·18	1·37	0·13	0·11	1·03	0·01	—
Oak	60·0	1·96	0·07	0·01	0·08	0·95	0·16	0·09	0·61	—	—
Scotch fir	55·0	0·63	0·06	—	0·06	0·26	0·13	0·03	0·08	0·03	—
Spruce	55·0	2·63	0·04	—	0·06	0·40	0·21	0·07	1·84	—	—
VII. *Manufactured Products.*											
Fine wheat flour	13·6	0·41	0·15	0·01	0·03	0·01	0·21	—	—	—	—
Wheat bran	13·5	5·56	1·33	0·03	0·94	0·26	2·88	—	0·06	—	—
Rye flour	14·2	1·69	0·65	0·03	0·14	0·02	0·85	—	—	—	—
Rye bran	13·1	7·14	1·93	0·09	1·13	0·25	3·42	—	—	—	—
Barley flour	14·0	2·00	0·58	0·05	0·27	0·06	0·95	0·06	—	—	—
Maize meal	14·0	0·95	0·27	0·03	0·14	0·06	0·43	—	—	—	—
Malt	4·2	2·66	0·46	—	0·22	0·10	1·07	—	0·88	—	—
Malt dust	9·2	5·96	2·08	—	0·08	0·09	1·25	0·38	1·77	—	—
Beer	90·0	0·39	0·15	0·03	0·02	0·01	0·13	0·01	0·04	0·01	—
Wine	86·6	0·28	0·18	—	0·02	0·02	0·05	0·01	0·01	—	—
Linseed cake	11·5	5·52	1·29	0·08	0·88	0·47	1·94	0·19	0·36	0·03	—
Cotton-seed cake	11·5	6·15	2·18	—	0·26	0·28	2·95	0·07	0·25	—	—
Potato skins	30·0	6·71	4·83	0·05	0·45	0·64	0·23	0·03	0·18	0·14	—
Buckwheat groats	14·0	0·62	0·16	0·04	0·08	0·01	0·30	0·01	—	0·01	—
VIII. *Wood (air-dried).*											
Apple tree	15·0	1·10	0·13	0·02	0·06	0·78	0·05	0·03	0·02	—	—
Beech, trunk	15·0	0·55	0·09	0·02	0·06	0·31	0·03	0·01	0·03	—	—
Beech, brushwood	15·0	1·23	0·17	0·03	0·13	0·59	0·15	0·01	0·12	—	—
Birch	15·0	0·26	0·03	0·02	0·02	0·15	0·02	—	0·01	—	—
Grape	15·0	2·34	0·70	0·16	0·16	0·87	0·30	0·06	0·02	0·02	—
Mulberry	15·0	1·37	0·09	0·20	0·08	0·78	0·03	0·14	0·05	0·06	—
Larch	15·0	0·27	0·04	0·02	0·07	0·07	0·01	0·01	0·01	—	—
Oak	15·0	0·51	0·05	0·02	0·02	0·37	0·03	0·01	0·01	—	—
Scotch fir	15·0	0·26	0·03	0·01	0·02	0·13	0·02	0·01	0·04	—	—

Nickel.—Minute amounts of nickel are of general occurrence in plants and in many tissues of the animal body, *e.g.* pancreas and bones ("Bibliography of the More Important Heavy Metals Occurring in Food and Biological Material," Society of Public Analysts, 1934, 24). K. Scharrer and W. Schropp (Z. Pflanz. Düng. 1933, A, **31**, 94) reported growth increases resulting from the addition of nickel to many plants.

Phosphorus.—Phosphorus always makes up an important fraction of plant ash, the percentage calculated as P_2O_5 varying between 5 and 20. It is a constituent of all proteins and is, therefore, an essential element both in plants and animals. In animals, as calcium phosphate, it is the main constituent of bones, and phosphorus occurs in relatively large amount in the brain.

Potassium.—Potassium is essential for the growth of all plants, and, as its name implies, has for a long time been recognised as the most abundant element in plant ash. As far as is known, it is present in plants entirely in soluble form.

Rubidium.—Rubidium is of common occurrence in minute amounts in plants (W. A. Robinson, L. A. Steinkoenig, and C. F. Miller, U.S. Agric. Dept. 1917, Bull. 600). O. Loew (Chem.-Ztg. 1913, **37**, 61) reported that RbCl in small doses caused increased growth in plants. C. H. Boissevain (J. Infectious Diseases, 1928, **43**, 194) found that rubidium or uranium, but not lithium, sodium, or cæsium, could replace potassium in culture solutions, he therefore concluded that plants require the rays emitted by potassium, rubidium, or uranium.

Selenium.—Selenium is of common occurrence in minute amount in plants, and in such conditions has a beneficial effect (J. Stocklasa, Biochem. Z. 1922, **130**, 604 ; V. E. Levine, Amer. J. Bot. 1925, **12**, 82).

Silicon.—Plant ash always contains silica, the percentage varying widely (between 1% or less to 50% or even more).

There is no definite proof that silicon is an essential element for plants, but there are records of increased growth and of increased resistance to fungus diseases and insect attack resulting from the addition of silicates to soils and culture solutions. References to the literature are given by R. S. Young (Cornell Univ. Agric. Exp. Sta. Mem. 1935, 174).

Silver.—The presence of traces of silver has been recorded in mushrooms by H. Ramage (Nature, 1930, **126**, 279), and in all parts of apple trees by W. A. Roach (Annual Report East Malling Research Station for 1928-1930, 1931, 101). G. Bohn and A. Drzewina (Compt. rend. Soc. Biol. 1932, **109**, 638) have recorded increased plant growth resulting from contact with metallic silver.

J. H. Sheldon and H. Ramage (Biochem. J. 1931, **25**, 1608) detected traces of silver in many, and Zbinden (Mem. Soc. Vand. Sci. Nat. 1930, **3**, 233) in all organs of the human body.

Sodium.—Sodium is of universal occurrence in plants, the percentage Na_2O in plant ash varying between 0·02 and 20. There is no evidence that sodium is essential to any plants, but application of sodium salts to certain soils liberates potassium from the soil particles into the soil solution, whence it is available to plants. Plants which normally inhabit the sea-shore or salt marshes, and others bred from them, such as mangolds and sugar beet, appear to be able to utilise sodium directly ; but even in these plants sodium cannot entirely replace potassium.

Sodium is present in all organs of the animal body.

Strontium.—W. O. Robinson, L. A. Steinkoenig, and C. P. Miller (U.S. Dept. Agric. Bull. 1917, 600) and G. Bertrand and L. Silberstein (Compt. rend. 1928, **186**, 477) reported the presence of traces of strontium in numerous plants. J. S. McHargue (J. Agric. Res. 1919, **16**, 183) reported increased yields of plants due to the addition of strontium salts. D. Burk and H. Lineweaver (Arch. Mikrobiol. 1931, **2**, 155) stated that either calcium or strontium was essential for the nitrogen fixation process of *Azotobacter*, but that the bacterium could grow in the absence of these elements if certain other elements such as magnesium, barium, or beryllium were present in sufficient concentration.

Tin.—Traces of tin have been detected in marine algæ by E. Cornec (Compt. rend. 1919, **168**, 513) and in apple trees by W. A. Roach (Annual Report East Malling Research Station for 1928–1930, 1931, 101).

G. Bertrand and Cinrea (Compt. rend. 1931, **192**, 780 and 990) reported that tin is a normal constituent of animal tissue.

Further references will be found in "Bibliography of the More Important Heavy Metals Occurring in Food and Biological Material" (Society of Public Analysts, 1934, 26).

Titanium.—The presence of small amounts of titanium in numerous plants has been recorded by G. Bertrand and C. Voronca-Spirt (Compt. rend. 1929, **188**, 1199 ; Bull. Soc. chim. 1930, [iv], **47**, 102), who found that there was most titanium in the chlorophyll-containing parts of the plants.

H. O. Askew (New Zealand J. Sci. Tech. 1930, **12**, 173) found an association between bush sickness of animals and low titanium content of pasture.

Vanadium.—The presence of vanadium in apple trees was reported by W. A. Roach (Annual Report East Malling Research Station for 1928–1930, 1931, 101). Growth increases due to the addition of vanadium have been reported in oats by V. A. Kryukov (Amer. Chem. Abstr. 1932, **26**, 1373), in algæ by H. Bortels (Arch. Mikrobiol. 1930, **1**, 333), and in *Azotobacter* in culture solution by K. Konishi and T. Tsuge (J. Agric. Chem. Soc. Japan, 1933, **9**, 129).

Zinc.—Zinc is now recognised as a normal constituent both of animals and plants. "The Bibliography of the More Important Heavy Metals Occurring in Food and Biological Material" (Society of Public Analysts, 1934, 27) contains 94 references. Usually the metal occurs in small amount only, but a few plants, which will grow only in soils rich in zinc, give ashes which contain relatively high percentages of the metal ; *Viola tricolor*, var. *calaminaria* and *Thlaspi alpestre*, var. *calaminaria* are examples.

A. L. Sommer and C. B. Lipman (Plant Physiol. 1926, **1**, 231) and A. L. Sommer (*ibid.* 1928, **3**, 217 ; Amer. Fertilizer, 1930, **72**, 15) found zinc essential for the growth of barley, sunflowers, buckwheat, and beans in water culture.

Zinc sulphate has been used successfully against rosette of pecan, walnut, pear, citrus, apple, and other trees ; it was successful when applied to the soil, sprayed on the leaves in solution or injected in solution through holes in the trunk or simply placed as dry solid in the holes. References to the literature are given in Imperial Bureau of Soil Science, 1934, Technical Communication 31, 28.

A. H. Finch and A. F. Kinnison (Arizona Agric. Expt. Sta. 1933, Tech. Bull. 47, 407) found that rosetted trees contained less zinc than normal ones and that the incidence of rosette on irrigated land in the south-western United States was associated with lack of zinc in the irrigation waters. W. A. R.

Importance of the Ash Constituents of Foods.—The influence of the mineral matter in the food of animals upon their health and well-being is probably much greater than is generally recognised. Not only is it essential that all the inorganic constituents required for building up the tissues and producing the various digestive and other secretions be supplied in sufficient quantities, but it is important, at least with certain pairs of constituents, that they be supplied in appropriate ratios to each other.

A preponderance of phosphoric acid over lime and magnesia in the diet is probably the cause or a predisposing cause of certain diseases of the bones of horses, mules, and donkeys (Ingle, J. Comp. Pathology and Therapeutics, 1907 ; J. Agric. Sci. 1908, **3**, 22 ; J. Roy. Inst. Public Health, 1909) ; while the ratio of potash to soda in the food has an important bearing upon health, and especially upon the susceptibility to certain diseases, *e.g.* scurvy.

The cereals contain a large excess of phosphoric acid over lime, and the use of an exclusively cereal diet may lead to imperfect bone nutrition.

The necessity of an adequate supply of chlorides in the diet is well recognised, and in many countries the ordinary food supplies of domestic animals have to be supplemented by common salt to ensure healthy existence.

Whenever the rations are restricted to one or two items, there is considerable probability that certain mineral constituents will be lacking or supplied in improper proportions.

It is too often the practice, in discussing the feeding of animals, to devote much consideration to the organic portions of their food, but beyond requiring that sufficient mineral matter or " bone-forming " material be present, to pay little or no attention to its composition.

Thus bran is widely regarded as a food particularly rich in mineral matter, and therefore valuable for bone nutrition ; but the ratio of phosphorus pentoxide to lime in this food is about 11 to 1, and the practice of feeding animals largely upon bran is known to produce a disease of the bones—" bran rachitis " in horses.

Kellner (" Scientific Feeding of Animals," 1909) estimates that for oxen 50 g. of phosphorus pentoxide and 100 g. of lime per 1,000 kg. body weight per day are required in the food, while for full-grown sheep 1 g. of the former and 11 g. of lime suffice.

In England, fortunately, hay—either meadow or clover—forms a large part of the rations of farm animals, and this contains a large excess of lime over phosphoric acid, and thus neutralises the opposite preponderance in the grain or cake used with it.

But in South Africa and perhaps some other countries, meadow or clover hay is but little used, and many horses are fed entirely upon oat hay or oat hay and maize. In either case there is a large preponderance of phosphoric acid over lime, and to this fact the prevalence of certain bone diseases is almost certainly due.

Similar considerations apply to other animals kept in confinement, especially to poultry when deprived of a grass run, and to pigs.

ASHBURY METAL *v.* ANTIMONY, ALLOYS OF.

ASIPHYL *v.* ASYPHIL.

ASMANIT. Activated bleaching earths used in refining petroleum.

ASPARAGINASE converts asparagine into aspartic acid and ammonia. It also attacks glutamine, but no other amides. The optimum p_H value being 8–8·5, formol titration is used to follow its action. (Geddes and Hunter, J. Biol. Chem. 1928, **77**, 197). It has a fairly wide distribution in animals, particularly in the liver, and is present in young *Vicia sativa* plants, etc., also in yeast and *Aspergillus* (Bach, Compt. rend. 1928, **187**, 955). E. F. A.

ASPARAGINE. *Aminosuccinamic acid*, $CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CO{\cdot}NH_2$, occurs in two optically active forms, differing in direction of rotatory power and in taste. *Lævo-asparagine*, discovered by Vauquelin and Robiquet (Ann. Chim. 1806, **57**, 88) in the young shoots of asparagus (*Asparagus officinalis*, Linn.), is widely distributed in the vegetable kingdom, occurring in most plants at the time of budding and during the flowering period, and, with glutamine, forms the chief non-protein compounds present in the juice of ripening oranges (Scurti and de Plato, Chem. Zentr. 1908 [ii], **16**, 1370 ; Stieger, Z. physiol. Chem. 1913, **86**, 245, 269 ; Smolenski, Z. Ver. deut. Zucker-Ind. 1911, 435 ; Tutin, J.C.S. 1913, **103**, 1274 ; Chapman, *ibid.* 1914, **105**, 1901 ; Tutin and Clewer, *ibid.* 570). It is also found in blood (Abderhalden, Z. physiol. Chem. 1913, **88**, 478). Miyacha (Bull. Coll Agric. Tokyo, 1897, **2**, 458) has shown that in the case of *Pæonia albiflora* and *Thea chinensis*, even old leaves, showing incipient decay, can produce asparagine. It occurs to a larger extent in leguminous plants than in any other natural order, and is most abundant at the time of germination, the quantity being greater in etiolated than in normal plants (Borodin, Bied. Zentr. 1879, 357 ; *see also* Ritman, Izv. Moskow. Selsk. Khoz. Inst. **18**, 212 ; from Amer. Chem. Abstr. 1913, 3144 ; Nicolaieva, Bull. Agr. Intelligence, 1917, **8**, 204). Sachsse

(Landw. Versuchs-Stat. 1874, **17**, 88) found that the amount of asparagine in germinating peas increased from 0·67 to 6·94% during 24 days' growth ; and Schulze and Umlauft (*ibid.* 1875, **18**, 1) found 17·9% of asparagine in the dried shoots of *Lupinus luteus* seedlings germinated in the dark in distilled water (*cf. also* Mercadante, Gazzetta, 1875, **5**, 187 ; Schulze, Landw. Versuchs-Stat. 1895, **46**, 383 ; Stoklasa, Landw. Jahrb. 1895, **24**, 827 ; Bourquelot and Herissey, J. Pharm. Chim. 1898 [vi], **8**, 385 ; Bréal, Ann. agron. 1900, **26**, 5 ; Schulze and Barbieri, Landw. Versuchs-Stat. 1878, **21**, 63 ; Kinoshita, Bull. Coll. Agric. Tokyo, 1895, **2**, 203 ; Schulze and Bosshard, Z. physiol. Chem. 1885, **9**, 420 ; Bungener, Bied. Zentr. 1885, 861 ; Behrens, Bot. Zentr. 1894, 178). Asparagine is one of the decomposition products of proteins (Schulze, Bied. Zentr. 1901, **30**, 106 ; Chem. Zentr. 1901 [i], 1108 ; Ber. deut. bot. Ges. 1907, **25**, 213), and has been isolated from the products of hydrolysis of edestin by the successive action of pepsin, trypsin, and yeast dipeptidase (Damodaran, Biochem. J. 1932, **26**, 235). Its accumulation in the plant during the periods of germination and budding, particularly when the development occurs in the dark, is attributed by Borodin (Bied. Zentr. 1879, 357) and Schulze and Barbieri (J. pr. Chem. 1882 [ii], **25**, 145), to the absence of carbohydrates which under conditions of normal assimilation effect the reincorporation of amides into protein molecules ; and this view is confirmed by Monteverde (Ann. agron. 1892, **17**, 376), who found that branches of lilac plunged in distilled water or 4% glycerol solution and kept in the dark contained abundance of asparagine at the end of 15 days, but neither starch nor mannitol. When, however, branches of the same plant were kept in solutions of glucose, sucrose, or mannitol, they formed no asparagine in a month, but contained much mannitol and starch. Another source of asparagine in the plant is its synthetic formation from ammonium salts, urea or nitrates supplied by the soil. This synthetic production is only possible in the presence of sugar, and under conditions that exclude the formation of proteins (Suzuki, Bull. Coll. Agric. Tokyo, 1897, **2**, 409).

Kinoshita (Bull. Coll. Agric. Tokyo, 1895, **2**, 196) found that young shoots of soya bean that showed an increase in asparagine, from 21·5 to 28·7% after four weeks' natural growth, became poorer in asparagine (18·9–13·7%) if grown for the same period in 1% methyl alcohol or glycerol solution, but contained reserve protein. The view that asparagine is the chief form in which nitrogen is translocated in the plant (Schulze, Z. physiol. Chem. 1911, **71**, 31) is further supported by the observation of Vickery (J. Biol. Chem. 1925, **65**, 657) that asparagine is the most important constituent of the simple nitrogenous compounds in lucerne, although in rye Kiesel found aspartic acid but no asparagine (Z. physiol. Chem. 1924, **135**, 61). According to Ciamician and Ravenna (Atti R. Accad. Lincei, 1911 [v], **20**, 1, 614), there is an increase of alkaloid in the tobacco plant and date when supplied with asparagine. Morgen, Beger, and Westhausser (Landw. Versuchs-Stat. 1911, **75**, 265), experimenting with sheep, claim that, given a sufficiency of carbohydrate, a deficiency of protein may be made good with ammonium acetate and asparagine.

Asparagine can be extracted from the juice expressed from young vetch seedlings that have germinated in the dark, 10 kg. of vetch yielding 150 g. of pure asparagine (Piria, Annalen, 1848, **68**, 343). Sure and Tottingham found that asparagine is made use of in the nitrogen metabolism of etiolated pea plants (J. Biol. Chem. 1916, **26**, 535).

Asparagine crystallises from aqueous solution in large rhombic lævo-hemihedral prisms, *a* : *b* : *c* : : 0·4752 : 1 : 0·8294 (Freundler, Compt. rend. 1897, **125**, 657), containing $1H_2O$, which it loses at 100°, and then melts at 234°–235° (Michael, Ber. 1895, **28**, 1629) ; it has a sp.gr. 1·5434 at 14·8°/4° (Piutti, Gazzetta, 1904, **34**, 36) ; the molecular heat of combustion is 448·4 kg.-cal., and the heat of formation 205·1 Cals. (Berthelot and André, Compt. rend. 1890, **120**, 884 ; *see also* Emery and Benedict, Amer. J. Physiol. 1911, **28**, 301) ; it is sparingly soluble in cold, readily so in hot water—1 part dissolves in 82 parts of water at 10°, in 47 parts at 20° (Becker, Ber. 1881, **14**, 1028), in 58 parts at 13°, and 1·89 parts at 100° (Guareschi, Gazzetta, 1876, **6**, 370 ; *cf.* Bresler, Z. physikal. Chem. 1904, **47**, 611). The aqueous solution is weakly acid, has an insipid and disagreeable taste, and is lævo-rotatory $[\alpha]_D - 5°4'$ (Piutti, Compt. rend. 1886, **103**, 134) ; the rotatory power of the solution is increased by raising the temperature and by the addition of alkalis, reversed by mineral acids and by solutions of certain inorganic salts, and destroyed by acetic acid (Champion and Pellet, Compt. rend. 1876, **82**, 819 ; Becker, Ber. 1881, **14**, 1028 ; Smolenski, Z. Ver. deut. Zucker-Ind. 1910, 215 ; and 1912, 791 ; Pellet, Z. Ver. deut. Zucker-Ind. 1911, 435 ; Clough, J.C.S. 1915, **107**, 1513 ; Andrlik and Staněk, Z. Zuckerind. Böhm. 1907, **31**, 417). Advantage is taken of this last fact to eliminate the error due to the presence of asparagine in saccharimetric determinations of sugar liquors from beets and canes. Asparagine is partially hydrolysed by boiling with water, forming *aspartic acid* (*aminosuccinic acid*),

$$C_2H_3(NH_2)(CO_2H)_2,$$

and ammonia ; the change is rapid and complete when excess of barium hydroxide or dilute hydrochloric or sulphuric acid is employed (Schulze, Landw. Versuchs-Stat. 1884, **29**, 233) ; by the action of potassium permanganate, asparagine is oxidised to urea and ammonia ; and when used in 5% aqueous solution for the culture of *Bacillus pyocyaneus*, it is converted into aspartic acid after 60 hours, and completely decomposed after 72 hours (Arnaud and Charrin, Compt. rend. 1891, **112**, 755 ; Adeney, Proc. Roy. Irish Acad. 1905, **25**, 6). An aqueous solution in presence of sunlight yields acetaldehyde, ammonia, and carbon dioxide (Ganassini, Giorn. Farm. Chim. 1912, **62**, 439). Under the action of enzymes, asparagine yields a mixture of formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Z. 1909, **18**, 424), and a similar change is effected by brewer's yeast (Effront, Mon. Sci. 1909 [iv], **23**, i, 145 ; and Kurono, J. Coll. Agric. Tokyo, 1911, **1**, 295).

The estimation of asparagine is based upon its quantitative conversion into aspartic acid and ammonia by the action of hydrochloric acid; the aspartic acid may be removed in the form of its sparingly soluble copper salt (Engel, Compt. rend. 1888, **106**, 1734) and the ammonia determined by Sachsse's method (J. pr. Chem. 1872 [2], **6**, 118) or by one of the modifications of Schloesing's method described by Meunier (Ann. agron. 1881, **6**, 275), by Schulze (J. pr. Chem. 1885 [2], **31**, 233), or by Brown and Millar (J.S.C.I. 1904, 135). Palet (Anal. Asoc. Quím. Argentina, 1917, **5**, 95) points out that the results of the estimation by Schloesing's method are influenced by the employment of different alkalis.

For the estimation of asparagine in the presence of glutamine, *see* Chibnall and Westall (Biochem. J. 1932, **26**, 122).

Asparagine has feeble basic and acidic properties, and forms salts with acids and bases (Chautard and Dessaigne, Annalen, 1848, **68**, 349 ; 1852, **82**, 237 ; Smolka, Monatsh. 1887, **6**, 915) ; it also forms double compounds with certain salts of the heavy metals ; the sparing solubility of the compound with mercuric nitrate is made use of in isolating small quantities of asparagine from solutions containing carbohydrates (Schulze, Ber. 1882, **15**, 2855) ; it forms stable complex internal salts with certain heavy metals ; the chromium salt,

$$Cr(C_4H_7O_3N_2)_3,$$

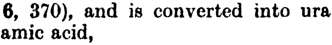
crystallises in microscopic rose-violet needles (Tschugaeff, Serbin, Compt. rend. 1910, **151**, 1361); it combines with copper hydroxide to yield a copper complex of the formula,

$$Cu(C_4H_7O_3N_2)_2,$$

(Kober and Sugiura, J. Biol. Chem. 1912, **13**, 1) ; the *alum*,

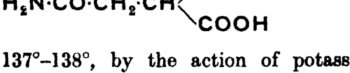
$$(C_4H_8O_3N_2)_2H_2SO_4,Al_2(SO_4)_3,24H_2O,$$

forms octahedral crystals. Asparagine is converted into *l*-chlorosuccinic acid and fumaric acid by the action of nitrosyl chloride in hydrochloric acid solution (Tilden and Forster, J.C.S. 1895, **67**, 489) ; it yields the amide of uramidosuccinic anhydride,



$$H_2N{\cdot}CO{\cdot}CH_2{\cdot}\underset{\displaystyle CO}{CH}{\cdot}NH{\cdot}CO{\cdot}NH$$

when fused with urea (Guareschi, Gazzetta, 1876, **6**, 370), and is converted into uramidosuccinamic acid,



$$H_2N{\cdot}CO{\cdot}CH_2{\cdot}CH\begin{cases}NH{\cdot}CO{\cdot}NH_2\\COOH\end{cases}$$

m.p. 137°–138°, by the action of potassium cyanate (Guareschi, Ber. 1877, **10**, 1747). Certain condensation products of asparagine with other amino-acids are described by Fischer (Ber. 1904, **37**, 4585 ; 1907, **40**, 2048), *chloroacetylasparagine*, m.p. 148°–149° (corr.) ; *glycylasparagine*, m.p. 216°, $[\alpha]_D$ −6·4° at 20° ; *anhydroglycylasparagine*, decomposing at 274° ; d-*leucyl*-l-*asparagine*, decomposing at 230° (corr.), $[\alpha]_D$ −53·6° at 20° ; l-*leucyl*-d-*asparagine*, m.p. 228° (corr.), $[\alpha]_D$ +17·8° ; *asparagylaspartic acid*, decomposing at 120°. Sasaki (Beitr. Chem. Physiol. Path. 1907, **10**, 120) describes a *benzoylpolypeptide* of asparagine, $C_{19}H_{24}O_8N_6$, decomposing at 210°, and giving the biuret reaction.

Benzyl hydrogen asparagine dithiocarboxylate,

$$CO_2H{\cdot}C_2H_3(CO{\cdot}NH_2){\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph,$$

has m.p. 180°. The barium salt crystallises in slender needles (Siegfried and Weidenhaupt, Z. physiol. Chem. 1910, **70**, 152).

As regards the alimentary value of asparagine, it has been found that in the case of herbivorous mammals and geese, asparagine has a protein-sparing action, and under appropriate conditions prevents waste and causes the formation of protein (Weiske, Bied. Zentr. 1879, 744 ; 1882, 312 ; Z. Biol. 1879, **15**, 261 ; 1885, **20**, 276 ; Landw. Versuchs-Stat. 1888, **34**, 303 ; Rosenfeld, Z. Ver. deut. Zucker-Ind. 1900, 1055, from J.S.C.I. 1901, **20**, 271). According to Zuntz and Müller (Pflüger's Archiv, 1906, **112**, 245), the protein-sparing action of asparagine is the result of a kind of symbiosis, the bacteria in the paunch of the ruminants decomposing the asparagine in preference to the protein in the food. In the case of omnivora and carnivora, asparagine exerts only a diuretic action (Murck and Voit, Bied. Zentr. 1884, 749 ; Politis, Z. Biol. 1893, **27**, 492 ; Mauthner, *ibid.* 507 ; Gabriel and Voit, *ibid.* **29**, 115, 125 ; Levene and Kober, Amer. J. Physiol. 1909, **23**, 324 ; *see*, however, Abderhalden, Z. physiol. Chem. 1911, **74**, 481 ; and Nitsche, Beitr. Phys. 1914, **1**, 53).

Dextro-asparagine was discovered by Piutti (Ber. 1886, **19**, 1691) in the young shoots of the vetch (*Vicia sativa*, Linn.). 6,500 kg. of vetch buds yielded 20 kg. of crude asparagine, from which 100 g. of pure dextro-asparagine was isolated ; it is slightly more soluble than the lævo-compound ; the solution has an intensely sweet taste, is dextro-rotatory in neutral or alkaline solution $[\alpha]_D$ +5·41° (Piutti, Compt. rend. 1886, **103**, 134), and lævo-rotatory in acid solution ; it forms large rhombic dextro-hemihedral crystals, *a* : *b* : *c* : : 0·4741 : 1 : 0·8310 (Freundler, Compt. rend. 1897, **125**, 657). A solution of equal parts of the two optically active asparagines is optically inactive, but the two varieties separate on crystallisation, twinning frequently taking place between the left and right crystals (Piutti, *l.c.* 1886, **103**, 134). *d*- and *l*-Asparagine can be separated by fractional crystallisation from hot water, although both have the same solubility at 20°. The solubility of *l*-asparagine, previously heated, is at least doubled after cooling, and only slowly returns to its original value (Erlenmeyer, Biochem. Z. 1913, **52**, 439). The silver salt of dl-*asparagine*, $C_4H_7O_3N_2Ag$, forms wart-like clusters of crystals, m.p. 182°–183° (decomp.) (Abderhalden and Kautzsch, Z. physiol. Chem. 1912, **78**, 115).

According to Pringsheim (Z. physiol. Chem.

1910, **65**, 89), the *d*-asparagine found by Piutti in the mother liquors from which the *l*-asparagine had been isolated was formed by the racemisation of the *l*-asparagine during the process of evaporation of the solutions. The author states that after boiling *l*-asparagine, $[\alpha]_D^{20°}$ $+36{\cdot}19°$ in $N/10$ hydrochloric acid solution, for 12 hours, with water, and subsequent fractional crystallisation, he obtained a fraction that had $[\alpha]_D^{20°}$ $-15{\cdot}3°$ in $N/10$ hydrochloric acid solution, and therefore contained *d*-asparagine.

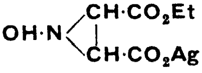
In addition to the two asparagines already described, there is a third form known as α-asparagine ; it does not occur naturally ; is optically inactive, crystallises in the triclinic system, $a : b : c = 1{\cdot}5957 : 1 : 0{\cdot}5668$; $\alpha = 91° 19'$, $\beta = 113° 12'$, $\gamma = 83° 48'$ (Brugnatelli) ; and has a sp.gr. 1·454 at 14·8°/4° (Piutti, Gazzetta, 1904, **34**, ii, 36), and is not structurally identical with the optically active or β-asparagines. The three asparagines have been synthesised by Piutti (Gazzetta, 1887, **17**, 126 ; 1888, **18**, 457) by the following methods, that leave no doubt as to the constitution of the compounds. By the reduction of the oxime of oxalacetic ester, $CO_2Et{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$, with sodium amalgam and partial saponification of the product, Piutti obtained two different ethyl hydrogen aspartates, melting at 165° and 200° respectively. The ester melting at 165° is identical with the compound obtained by reducing Ebert's (Annalen, 1885, **229**, 45) monoethyl ester of oximinosuccinic acid, which has the formula $CO_2H{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$, since on heating it loses CO_2 and forms oximinopropionic ester, $CH_3{\cdot}C(NOH){\cdot}CO_2Et$. It follows, therefore, that the ethyl hydrogen aspartate melting at 165° is the monoethyl α-aspartate, $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2Et$, and the ester melting at 200° must be the monoethyl β-aspartate, $CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CO_2Et$. When these esters are treated with alcoholic ammonia, they are converted into the corresponding asparagines ; the ester m.p. 165° gives inactive *α-asparagine*,

$$CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CONH_2,$$

and the ester m.p. 200° yields a mixture of *d*- and *l*- β-asparagines,

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CONH_2$$

From silver ethyl γ-oximinosuccinate,



$$\mathrm{OH{\cdot}N}\Big\langle\begin{array}{l}\mathrm{CH{\cdot}CO_2Et}\\ \;|\\ \mathrm{CH{\cdot}CO_2Ag}\end{array}$$

Piutti (Gazzetta, 1890, **20**, 402) obtained a mixture of the three asparagines, the α-asparagine readily gave up its water of crystallisation in a vacuum, and fell to powder ; and the β-asparagines could then be separated by hand sorting. A mixture of the three asparagines was also obtained by the action of alcoholic ammonia on the ethyl hydrogen ester of inactive aspartic acid (Piutti, Gazzetta, 1887, **17**, 126 ; 1888, **18**, 457). Körner and Menozzi (Gazzetta, 1887, **17**, 171, 226) effected the synthesis of the *d*- and *l*- β-asparagines from ethyl bromosuccinate, ethyl fumarate or ethyl maleate, by the action of alcoholic ammonia ; and similar results were obtained by Piutti (Ber. 1896, **29**, 2069) with *l*-bromo-succinamic acid or maleic anhydride.

β-Ethylasparagine,

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NHEt,$$

m.p. 258°–260°, with decomposition, and *β-allylasparagine*,

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_3H_4,$$

melting and decomposing at 258°–261°, prepared by the action of the corresponding alkylamine on ethyl β-aspartate, yield optically inactive solutions (Piutti, Gazzetta, 1888, **18**, 478).

M. A. W. and W. V. T.

ASPARAGUS. The young shoots of *Asparagus officinalis.* The fresh shoots are cooked as a vegetable and large quantities are now canned satisfactorily. Early claims of asparagus to high vitamin values seem to be unsupported by more recent work, except in the case of vitamin B for which this vegetable forms a very suitable source.[1] According to Sherman the average analysis of asparagus is :

	Water.	Protein.	Fat.	Carbo-hydrate.	Fibre.	Ash.
Fresh	94	1·8	0·2	3·3	0·8	0·7
Canned	94	1·5	0·1	2·8	0·5	1·2

Of the edible portion the ash constituents are : **Ca** 0·025, **Mg** 0·011, **K** 0·196, **Na** 0·007, **P** 0·039, **Cl** 0·039, **S** 0·041, **Fe** 0·001, values being calculated on a fresh weight basis.

The nitrogenous constituents include a relatively large proportion of asparagine. Coniferin and vanillin are present in the sap and tissue. Mannitol and a mannan have also been detected. The latter probably functions as a carbohydrate reserve in the seeds which contain no starch (Peters, Arch. Pharm. 1902, **240**, 53). Seeds also have approximately 15% of an oil characterised by sp.gr. 0·928 at 13° and an iodine value of 137·1. A. G. Po.

ASPARAGUS STONE *v.* Apatite.

ASPARTASE (in *B. coli*) acts in a reversible way ; it produces *l*-aspartic acid from fumaric acid as it catalyses the union with NH_3, and removes NH_3 from *l*-aspartic acid without hydrolysis (Quastel and Woolf, Biochem. J. 1926, **20**, 545 ; Woolf, *ibid.* 1929, **23**, 472).

E. F. A.

ASPARTIC ACID. *Aminosuccinic acid*, $CO_2H{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$, found in young sugar cane and in molasses of sugar beet (Scheibler, Jahresber. 1886, 399), in young shoots of the gourd (Schulze and Barbieri, Ber. 1878, **11**, 710), and in mulberry leaves (Mimuroto, J. Coll. Agric. Tokyo, 1912, **5**, 63), has been observed in diseased liver (Taylor, Z. physiol. Chem. 1901, **34**, 580), and occurs in a certain gland of *Tritonium nodosum :* the posterior portion of the gland when stimulated secretes an acid fluid from which aspartic acid immediately crystallises, and as aspartic acid is soluble in sea-water, it is probably employed by the animal in destroying the calcareous shells of the other shellfish that form its food (Henze, Ber. 1901, **34**, 348).

---

[1] Olliver found in ten samples of asparagus tips 0·900–1·460 (mean value 1·262) mg. per g. of ascorbic acid (vitamin C) (J.S.C.I. 1936, **55**, 153).

Aspartic acid is prepared by hydrolysing asparagine by means of hydrochloric or sulphuric acid, lime, baryta, lead oxide, or potash (Plisson, Ann. Chim. Phys. 1828 [2], **37**, 81; Schulze, Landw. Versuchs-Stat. 1884, **29**, 233); it is one of the degradation products of proteins, and is obtained when they are heated with dilute sulphuric acid (Kreussler, J. pr. Chem. 1869, **107**, 239; Ritthausen, *ibid.* 218; Fischer, Z. physiol. Chem. 1901, **33**, 151; 1902, **35**, 70; **36**, 462); or bromine or stannous chloride (Hlasiwetz and Habermann, Annalen, 1871, **159**, 325; 1873, **169**, 162). Aspartic acid is produced by the pancreatic digestion of fresh blood fibrin at 40°–50° (Radziejewski and Salkowski, Ber. 1874, **7**, 1050), or of gluten (Knieriem, Z. Biol. 1876, **11**, 198).

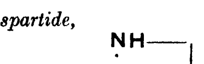
Aspartic acid can be synthesised by the action of boiling hydrochloric or nitric acid on the product obtained by heating the ammonium salts of malic, maleic, or fumaric acids (Dessaigne, Compt. rend. 1850, **30**, 324); by reducing and hydrolysing sodium ethyloximino-oxalacetate (Piutti, Chem. Zentr. 1888, 68); by condensing ethyl sodiophthalimidomalonate with ethyl chloroacetate and hydrolysing the product with hydrochloric acid (Dunn and Smart, J. Biol. Chem. 1930, **89**, 41); or by treatment of diethyl fumarate with alcoholic ammonia (Dunn and Fox, *ibid.* 1933, **101**, 493). The production of aspartic acid from ammonia and fumaric acid by *B. coli* is described by Quastel and Woolf (Biochem. J. 1926, **20**, 545).

The naturally occurring aspartic acid is lævo-rotatory and the same l-*aspartic acid* is obtained by hydrolysis of *lævo*-asparagine (Schiff, Ber. 1884, **17**, 2929); it crystallises in rhombic prisms. m.p. 270°–271° (Michael, Ber. 1895, **28**, 1629), is sparingly soluble in water—100 g. of water dissolve y mg. of the acid at $t°$, where

$$y = 372 + 14{\cdot}1t - 0{\cdot}18124t^2 + 0{\cdot}0053t^3$$

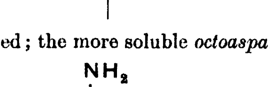
(Engel, Compt. rend. 1888, **106**, 1734). A solution containing 1·873% of acid is feebly dextro-rotatory below 75°, but lævo-rotatory above that temperature; *see also* Wood (J.C.S. 1914, **105**, 1992). In alkaline solutions the substance is strongly lævo-, and in acids strongly dextro-rotatory, and dextro-rotatory in aqueous solutions of certain inorganic salts (Becker, Ber. 1881, **14**, 1028). The rotatory power in acid and alkali reaches a maximum value under definite conditions of concentration (Wood, *l.c.*; Clough, J.C.S. 1915, **107**, 1510). The heat of combustion is 387·2 kg.-cal., the heat of formation 231·9 kg.-cal. (Berthelot and André, Compt. rend. 1890, **110**, 884); the heat of dissolution at 16° is −7·25 kg.-cal., heat of neutralisation by sodium hydroxide +3·0 kg.-cal. for the first, and +3·5 kg.-cal. for the second equivalent (Berthelot, Compt. rend. 1891, **112**, 829). Aspartic acid is readily soluble in aqueous solutions of certain mineral salts; for this reason Schiff (Ber. 1886, **17**, 2929) recommends that in its preparation from asparagine by boiling with hydrochloric acid, the minimum quantity (2 mols.) of acid be employed, and the excess afterwards neutralised by ammonia (1 mol.); by adopting this precaution, a yield of 90% of the theoretical is obtained. For the estimation of aspartic acid in the hydrolysis products of proteins, *see* Foreman (Biochem. J. 1914, **8**, 463).

Aspartic acid forms salts with acid and bases. The *copper* salt, $C_4H_5O_4NCu,4\frac{1}{2}H_2O$ or $C_4H_5O_4NCu,5H_2O$, forms pale-blue needles almost insoluble in cold water (Engel, *l.c.*; Abderhalden and Weil, Z. physiol. Chem. 1911, **72**, 23). The *calcium* salt can be precipitated quantitatively by means of alcohol (Foreman, *ibid.* 471). The mono-*silver* salt melts at 216°–217° with decomposition (Abderhalden and Kautzsch, Z. physiol. Chem. 1912, **78**, 123). A *uranyl* salt $UO_2(C_4H_5O_4N)_2,3H_2O$ is formed by double decomposition (Mazzucchelli and D'Alceo, Atti R. Accad. Lincei, 1912 [5], **2**, 11, 620). *Aspartic hydrochloride*, $C_4H_7O_4N{\cdot}HCl$, softens with gas evolution at 178°, and then does not alter up to 280° (Philippi and Uhl, Monatsh. 1913, **34**, 717). Aspartic acid is oxidised by hydrogen peroxide to the semi-aldehyde of malonic acid which breaks up into acetaldehyde and carbon dioxide (Dakin, J. Biol. Chem. 1909, **5**, 409); it is capable of furnishing the nitrogen required for the development of *B. coli communis* in presence of mannitol and glucose, becoming reduced to ammonium succinate (Harden, J.C.S. 1901, 623), and by enzyme action it is decomposed into formic, propionic and succinic acids (Neuberg and Cappezzuoli, Biochem. Z. 1909, **18**, 424; Borchardt, Z. physiol. Chem. 1909, **59**, 96; Abderhalden and Fodor, Z. physiol. Chem. 1913, **85**, 119, 130). On heating it with glucose under pressure Bauer and Barshall obtained succinic acid, and suggest that aspartic acid is the source of the succinic acid found in meat extract (Chem. Zentr. 1911, **2**, 1367). When aspartic acid is heated at 190°–200° for 20 hours, and the product boiled with water, two sparingly soluble anhydrides, *octoaspartide*,



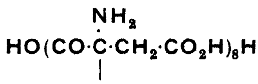
$$\mathrm{HO(CO{\cdot}\underset{|}{\overset{\overset{NH-\!\!-\!\!-}{\cdot}}{C}}{\cdot}CH_2{\cdot}\overset{|}{C}O)_8H},$$

and *tetraspartide*,



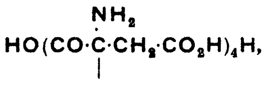
$$\mathrm{HO(CO{\cdot}\underset{|}{\overset{\overset{NH-\!\!-\!\!-}{\cdot}}{C}}{\cdot}CH_2{\cdot}\overset{|}{C}O)_4H},$$

are obtained; the more soluble *octoaspartic*,



$$\mathrm{HO(CO{\cdot}\underset{|}{\overset{\overset{NH_2}{\cdot}}{C}}{\cdot}CH_2{\cdot}CO_2H)_8H},$$

and *tetraspartic acid*



$$\mathrm{HO(CO{\cdot}\underset{|}{\overset{\overset{NH_2}{\cdot}}{C}}{\cdot}CH_2{\cdot}CO_2H)_4H},$$

can be isolated from the filtrate (Schiff, Ber. 1897, **30**, 2449). Dimethyl or diethyl sulphate and *l*-aspartic acid in alkaline solution give fumaric acid and alkylated ammonia derivatives (Novák, Ber. 1912, **45**, 834). The following alkyl esters of aspartic acid are described : *Monoethyl aspartate hydrochloride*, m.p. 199° ; *diethyl* and *dimethyl aspartate hydrochlorides*, deliquescent solids (Curtius and Koch, Ber. 1885, **18**, 1293 ; Wegscheiden and Frankl, Monatsh. 1906, **27**, 487), *ethyl β-aspartate*,

$$CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CO_2Et,$$

m.p. 200° ; *ethyl α-aspartate*,

$$CO_2H\cdot CH_2\cdot CH(NH_2)CO_2Et,$$

m.p. 165° (Piutti, Gazzetta, 1887, **17**, 126 ; 1888, **18**, 457). The methyl, ethyl, allyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl hydrogen esters are dextro-rotatory at ordinary and lævo-rotatory at higher temperatures, and form sparingly soluble copper salts (Piutti and Maghi, Gazzetta, 1906, **36**, ii, 738). *l*-Diethyl aspartate has b.p. 126·5°/11 mm. ; d^{17} 1·089 and $[\alpha]_{\mathrm{D}}^{20°}$ −9·46° (Fischer, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1900, **48**, 1062), or b.p. 126°–127°/10 mm., 150°–152°/25 mm., and forms a yellow *picrolonate*, $C_8H_{15}O_4N,C_{10}H_8O_5N_4$, m.p. 290° (Schmidt and Widman, Ber. 1909, **42**, 497). Aspartic acid and ethyl metaphosphate yield a derivative of the composition $C_6H_{12}O_7NP$ (Langheld, Ber. 1911, **44**, 2076). Aspartic acid forms a *p*-bromophenylcarbamido derivative, $C_{11}H_{11}O_5N_2Br$, m.p. 175°–176° (decomp.) (Hopkins and Wormall, Biochem. J. 1934, **28**, 228).

Of the *acyl* derivatives of aspartic acid, the *benzenesulphonyl* derivative,

$$PhO_2S\cdot NH\cdot C_2H_3(CO_2H)_2,$$

melts at 170° (Hedin, Ber. 1891, **23**, 3196) ; the *hippuryl* derivative,

$$BzHN\cdot CH_2\cdot CO\cdot NH\cdot C_2H_3(CO_2H)_2,$$

m.p. 191° (Curtius and Curtius, J. pr. Chem. 1904 [ii], **70**, 158) ; *benzoyl*-l-*aspartic acid*, m.p. 184°–185° (corr.), has $[\alpha]_{\mathrm{D}}^{20°}$ +37·4° ; *leucyl-aspartic acid*,

$$CH_2Pr^{\beta}\cdot CH(NH_2)\cdot CO\cdot NH\cdot C_2H_3(CO_2H)_2,H_2O,$$

decomposes at 180°–182° (corr.) (Fischer and Koenigs, Ber. 1904, **37**, 4585) ; and the *picryl* derivative, $C_{10}H_8O_{10}N_4$, has m.p. 137° ; *diethyl chloracetylaspartate*,

$$COOEt\cdot CH_2\cdot CH\cdot NH(CO\cdot CH_2Cl)COOEt,$$

(Fischer and Koenigs, Ber. 1904, **37**, 4585 ; Bornwater, Rec. trav. chim. 1917, **36**, 281) has m.p. 46°–47° ; b.p. 139° ; *aspartic diamide*, $C_2H_3(NH_2)(CONH_2)_2$, m.p. 131°, has $[\alpha]_{\mathrm{D}}$ −7°, and gives the biuret reaction (Fischer and Koenigs, *l.c.*). Aspartic acid resembles asparagine in its physiological action (Salkowski, Z. physiol. Chem. 1904, **42**, 1207 ; Andrlík and Velich, Z. Zuckerind. Böhm. 1908, **32**, 313).

d-*Aspartic acid*, obtained by hydrolysis of *d*-asparagine (Piutti, Ber. 1886, **19**, 1694), or from *l*-bromosuccinic acid and aqueous ammonia at −40°, a Walden rearrangement taking place (Fischer and Raske, Ber. 1907, **40**, 1051) ; is also obtained from a solution of the racemic acid [(*d*+*l*)-aspartic acid] which has been innoculated with a mould grown on *l*-aspartic acid (Engel, Compt. rend. 1887, **106**, 1734). *Benzoyl*-d-*aspartic acid*, obtained by Fischer (Ber. 1899, **32**, 2451) by the resolution of the racemic compound, through the brucine salts, has m.p. 181°–182°, $[\alpha]^{20°}$ −37·6° in alkaline solution.

Inactive (d+l)-*aspartic acid*, prepared by heating an aqueous solution of the hydrochloride of *l*-aspartic acid at 170°–180° for some hours (Michael and Wing, Ber. 1884, **17**, 2984) ; by heating *d*- or *l*-aspartic acid with 2 mols. HCl (sp.gr. 1·107) at 170°–180°, or from an aqueous solution of equal parts of the *d*- and *l*-acids, the racemic acid crystallises out (Piutti, Ber. 1886, **19**, 1694) ; (*d*+*l*)-Aspartic acid forms small monoclinic prisms ; 100 g. of water dissolve *y* mg. of the acid at *t*°, where,

$$y=517+21{\cdot}693t-0{\cdot}165t^2+0{\cdot}0079t^3$$

(Engel, Compt. rend. 1888, **106**, 1734). The *copper* salt, $CuC_4H_5O_4N,4\frac{1}{2}H_2O$, is dark-blue (Engel, *l.c.*). dl-*Aspartic acid picrolonate* forms long slender crystals with square ends decomposing at 130° (Levene and van Slyke, J. Biol. Chem. 1912, **12**, 127).. The *benzoyl* derivative has m.p. 164°–165° (corr.), and can be resolved into its active components by crystallising the brucine salt (Fischer, Ber. 1899, **32**, 2451).

M. A. W. and W. V. T.

ASPERULIN, m.p. 126°, $[\alpha]_{\mathrm{D}}$ −204·4°, is the glycoside of the woodruff *Asperula odorata.* The aglucone is unknown ; Hérissey (Compt. rend. 1925, **180**, 1695) describes it as similar to Aucubin, as it readily decomposes to a dark brown precipitate. Asperulin is also obtained from *Galium verum*, Lady's Bedstraw (Hérissey, *ibid.* 1927, **184**, 1674).

E. F. A.

ASPHALT AND BITUMEN. Bitumen is defined commercially as " mixtures of natural and pyrogenous hydrocarbons and of their non-metallic derivatives, which may be gaseous, liquid, viscous, or solid, but must be completely soluble in carbon disulphide." This definition covers a large number of different substances, but only those occurring naturally in association with mineral matter or those which can be manufactured into asphalt can be included under the heading " Asphaltic bitumen." Asphaltic bitumen is defined as " natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons by distillation or oxidation or cracking ; solid or viscous, containing a low proportion of volatile products ; possessing characteristic agglomerating properties and substantially soluble in carbon disulphide." Asphaltic bitumen is a very complex mixture of hydrocarbons together with their sulphur and nitrogen derivatives. Very little is known about its constitution, but it is believed to consist of colloidal carbon dispersed in heavy oil. It is generally thought that the petroleum oils which contain bitumen, including those from which the " natural " bitumens have been formed, result from the decay of marine organisms and plants. *Gilsonite*, sp.gr. 1·05–1·10, is one of the purest forms of bitumen which occurs in nature. It is black in colour with a conchoidal and lustrous fracture and is used in the manufacture of paints and varnishes. Asphaltic bitumen is prepared to-day by removing the lighter oils from certain crude petroleum oils by distillation in two stages: (1) at atmospheric pressure to remove the lighter fractions, and (2) in a vacuum of 28·5 in. of mercury. The process is carefully controlled to produce a bitumen of any desired penetration (J. S. Jackson, "Asphaltic Bitumen, its Properties and Applications," J. Oil and Col. Chem. Assoc. 1930, 304). Different asphaltic crude oils, such as those from Mexico, Venezuela, and Texas, yield bitumens of different properties, and also differ in their capacity to resist hardening under the effects of heat. Bitumen is used in the preparation of asphalt for road surfacing and for damp-coursing roofing and flooring in building construction. It is often used as a sealing medium for road surfaces and may be applied either hot or in the form of a dispersion in water. Roofing felt is made by saturating felt with bitumen. Other uses of bitumen include the manufacture of ebonite and of electrical insulating compounds. Methods for testing bitumen are given in "Standard Methods for Testing Petroleum and its Products," Institute of Petroleum Technologists, 3rd ed., 1935.

Asphalt is a mixture of bitumen with mineral matter, either prepared mechanically or occurring naturally. It occurs in the natural state in France, Switzerland, Italy, Germany and other countries in the form of asphalt rock, which is a limestone naturally impregnated with bitumen; there are no deposits in the United Kingdom. In some cases the rock is obtained from outcrop workings, but at St. Jean in France it is necessary to sink shafts to a depth of 1,000 ft. The bitumen was probably introduced at a later stage than the actual formation of the limestone as a petroleum oil carrying bitumen in solution; the lighter fractions have evaporated, leaving the bitumen behind.

Deposits of sand and sandstone containing up to 12% of a soft bitumen are found in Kentucky. Asphalt also occurs in the so-called "pitch lakes" of Bermuda and Trinidad, where asphaltic bitumen is admixed with a siliceous silt and clay. Asphalt is used in the manufacture of asphalt paving materials, which can be made on the one hand from natural asphalt alone or in conjunction with other materials, and on the other hand from purely artificial mixtures of asphaltic bitumen with mineral matter (Wilson, J.S.C.I. 1934, **53**, 924).

Compressed Asphalt is prepared from natural asphalt rock containing about 10% of bitumen ground to a fine powder, heated in rotating drums, and then spread while still hot on a concrete foundation and consolidated by ramming and ironing with hot irons. A non-skid finish can be applied at the time of construction by painting the surface of the partly consolidated material with a bitumen paint, covering the surface with a layer of bitumen coated granite chippings, and then ramming them into position with heavy iron "punners." The process is completed by rolling with a light roller as the material cools.

Powdered asphalt rock can be compressed into tile form in hydraulic presses to various shapes and thicknesses. For road-paving purposes, grooves may be moulded into the top surface of the tiles in order to provide a better grip for traffic. By mixing pigments with the asphalt powder coloured tiles can be manufactured for use when a decorative finish is required. Compressed asphalt and asphalt tiles are employed in paving roads which carry heavy city traffic.

Mastic Asphalt.—Natural asphalt rock is used in the preparation of mastic asphalt by mixing the powdered rock with asphaltic bitumen or fluxed Trinidad epuré. For road-paving purposes 35–45% of granite chippings are added. A plastic mixture is produced which is spread while hot with wooden floats on the surface to be covered.

"*Synthetic*" *Mastic Asphalt* is made from limestone and asphaltic bitumen. It is cheaper than that made from the natural product and although it can give good service it does not show such a high degree of stability under heavy traffic. It is impossible to secure such complete impregnation and coating of the limestone grains by artificial means, nor is the texture of the limestones generally available the same as that of the natural asphalt rock.

Mastic Asphalt for Building Purposes.—Mastic asphalt has been used in the building trade for more than sixty years for the roofing, flooring, and damp-coursing of important buildings. For this purpose the use of natural asphalt rock is to be preferred. The genuine material is often adulterated with limestone and methods have been devised for the detection of this adulteration (Wilson, Contract Journal, 1935, **112**, May 1st, Supplement V).

Rolled Asphalt.—A paving produced on a large scale to-day is prepared by mixing asphaltic bitumen, a filler, sand and granite chippings in a pug-mill type of mixer. The ingredients are mixed while hot, conveyed to the road, raked to the proper contour and consolidated by means of a heavy roller. Portland cement, ground limestone, chalk, clinker or slate dust have all given satisfactory results as fillers. Rolled asphalt may be laid in one layer, the thickness and composition being adjusted according to the traffic to be carried, but when the traffic is heavy a two-coat form of construction is desirable, a "carpet" layer being carried on a "binder" course made from bitumen, sand and comparatively large granite chippings (Wilson, J.S.C.I. 1932, **51**, 61–70). The surface can be given a roughened finish by rolling in granite chippings previously coated with bitumen. D. M. W.

ASPHODEL (Fam. *Liliaceæ*). *Asphodelus albus* and *A. fistulosus* grow in Southern Europe, and *A. kotschyana* in Asia Minor. The edible roots of these plants which contain much sucrose, starch, dextrin and mucilage are utilised for the preparation of alcohol and of adhesives.

ASPIDIN, ASPIDINOL *v.* Filix-mas.

ASPIDOSOMINE, ASPIDOSPERMATINE, ASPIDOSPERMINE *v.* Quebracho Alkaloids.

ASPIRATORS *v.* Pumps.

ASPIRIN, Acetosal, trade names of Acetylsalicylic acid, also termed xara, coxpyria, helicon, atonin, regipyrin, asposal, empirin, nupyrin, salcetin, salacetol, anglopyrin, salaspin aletodin. *Aspirin soluble,* calcium acetylsalicylate.

ASPIROPHEN. *Phenaspetin.* Amino-acet-*p*-phenetidine acetylsalicylate,

$$EtO\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH_2\cdot C_6H_4(OAc)CO_2H$$

ASPOSAL *v.* Aspirin.

ASPRIODINE. Acetyliodosalicylic acid, $AcO\cdot C_6H_3I\cdot COOH$.

ASSAYING. The term "assaying" (Fr. *essayer*) was originally applied to the testing of alloys and ores for their contents of gold and silver. A wider significance is now given to the word, and it is largely used to denote the partial or complete analysis of ores and metallurgical products. In this sense it includes what is more generally known as metallurgical analysis. Being an industrial operation, assaying differs from chemical analysis in that the primary consideration is cost and, consequently, speed. In certain cases where only comparative results are required, speed may be of the greatest importance and accuracy will have to be sacrificed to it. Such is often the case in the control of dressing plants and in the supervision of smelting operations. In general, the careful separations required in chemical analysis are omitted in favour of rapid direct determinations of the constituents required, and, in order to avoid delay, it is common practice to estimate several constituents by direct methods on separate samples.

The manipulation of the assayer differs from that of the chemist in only a few minor details. Calculation is minimised, in order to save time and avoid arithmetical error, by taking an exact weight of the sample, such as 0·5 or 1·0 g. The standard solutions for volumetric work are prepared in large quantity from salts of only commercial purity, the exact strength being determined periodically by standardisation against a pure metal or salt. These solutions are usually adjusted to such a strength that 1 ml. will be equivalent to an exact weight (*e.g.* 0·005 g.) of the metal to be determined, in order to simplify the subsequent calculation. In gravimetric work a factor weight is frequently taken, so that the weight of the product is multiplied by some simple figure, such as 5 or 10, to give the required percentage. The expenditure of much time and care in attaining a high degree of accuracy may be uneconomical, and consideration must be given both to the nature of the material under examination and to the probable magnitude of the sampling error. When assaying ores of the base metals, for example, an accuracy of $\pm 0{\cdot}1\%$ may suffice, whereas with gold ores the results should be correct to within 0·0003% (2 dwt. per ton) or less.

Sampling.—If the assay result is to be of any value, it is obvious that the sample provided must be representative, and considerable care and experience are required in attaining this object. The sampling of ores *in situ*, known as mine sampling, is outside the scope of this article, but consists, briefly, of taking a large number of small samples at regular intervals throughout the mass of the deposit, either by drilling or by sinking shafts and cutting drives through the ore body. The subsequent treatment of this first bulk sample is the same as that applied to shipments of ore. The general principle followed is to reduce both bulk and particle size by alternately dividing the material and crushing the separated portion. The fineness of crushing and the quantity of material reserved in each "cut" will depend upon the uniformity of the ore and the actual value. Fine crushing and the retention of a large sample at each stage is costly, but will give greater accuracy. For this reason ores which are to be treated in a crushed state (*e.g.* by flotation, cyanidation, etc.) should be sampled at as late a stage in the crushing operation as is convenient. When the ore is to be treated in lump form (*e.g.* ores for blast-furnace smelting) care must be taken to avoid the production of an excessive quantity of fine material.

When sampling large consignments the method of trenching is adopted. The ore is well mixed by shovelling and is then spread out into a square heap about 18–24 in. in depth. Trenches are dug through the heap in two directions at right angles, the material removed being taken as the sample. If a greater reduction in quantity is desired, samples may be taken from the sides of the trenches, at regular intervals, by means of a scoop, a cut being made in each case from the bottom to the top of the bank of the trench. This procedure may be repeated if the first cut is very large. The bulk having been reduced to a few hundredweights, the method of coning and quartering is next applied. The ore, further crushed if necessary, is thoroughly mixed, spread into a circle, and built up into a symmetrical cone round a vertical stick. This is done to avoid segregation of the finer material which would otherwise occur. This cone is flattened, a cross is marked on the surface of the heap, and two opposite quarters are rejected. The procedure is repeated, further crushing being carried out as necessary, until the sample is reduced to the required bulk.

Mechanical sampling devices are frequently installed in plants which handle crushed material. These are of many types, the general principle being to discharge the ore down a vertical or inclined chute, and to remove or deflect a section of the stream of ore, periodically, by mechanical means. Pulp is sampled in a similar manner. A receptacle of a suitable size is passed through the stream of pulp, from side to side, at regular time intervals. The sample is then filtered and dried.

A heap or vat of ore, tailings, etc., which must be sampled without being moved, is pierced at regularly spaced intervals by a sampling tube, which resembles a cheese taster and withdraws a cylindrical sample extending to the bottom of the material.

Further reduction of the sample is usually necessary when it arrives at the assay laboratory. This is effected by coning and quartering, or by the use of a machine known as a sample divider. The "Riffle" sample divider consists of a series of metal troughs with sloping bottoms arranged side by side, alternate troughs discharging in opposite directions into one of two receptacles. A falling stream of ore is thus halved, and can be further reduced as required. Miniature sampling machines of the automatic type, such as the "Knight" packet sampler, are used for the same purpose.

The final grinding of the ore is effected by means of a large cast-iron muller with a curved face, sliding on an iron bucking board, or by some form of mill, such as a disc grinding machine. The crushed ore is passed through a sieve, the fineness of which varies according to the class of the ore and the method of assay to be adopted. For a panning test a 30-mesh screen (*i.e.* one with 30 holes to the linear inch) suffices. For the fusion assay of lead concentrates a 60-mesh screen is used. Gold ores are normally crushed to 80- or 100-mesh for assay, but for very rich gold ores and for tin concentrates the best results are obtained after crushing to 120-mesh. Ores will sometimes require drying before they will pass through a fine screen. Moisture is then determined on the coarsely crushed ore by drying at about 105°C. on a steam bath, or, if the material will not be affected by a somewhat higher temperature, by heating on a sand bath. When crushing rich gold and silver ores, mint sweepings, etc., pieces of metal are found which have been flattened during crushing and are caught on the screen. These "metallics" are weighed and treated separately, and their value is calculated to the weight of material from which they were derived.

The dry, crushed sample is thoroughly mixed on a mixing cloth before weighing out the portion required for assay. When stored in a bottle or tin, any movement of the vessel causes segregation of the heavier particles, and a portion taken from the surface will not be representative.

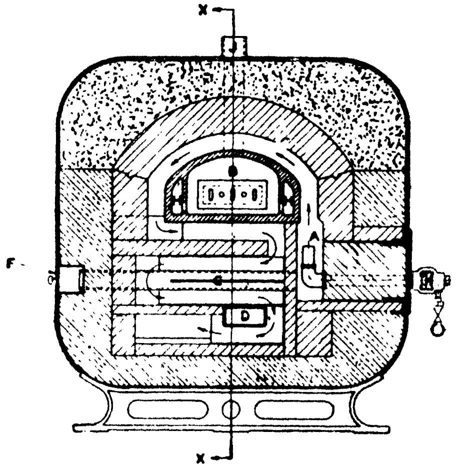
Metals and alloys are best sampled when in the molten state. This is done by taking a "dip" sample with a graphite sampling spoon, and either granulating the material so obtained or casting a small sample bar. Metallic ingots, pigs, bars, cakes, etc., are sampled by drilling, milling, sawing, or cutting a suitable quantity of the metal from certain arbitrary points. The points selected are those at which errors due to segregation are known to be minimised. Coins are sampled in various ways and require care, silver coins in particular being seldom uniform in composition. A simple method is to roll them thin and cut them into a large number of small pieces, so that all parts of the coin may be represented in the assay sample. Gold and silver wares have, usually, been pickled, and are richer on the surface than in the interior. It is necessary, therefore, to scrape away the surface before removing a portion of the metal for assay.

Metal drosses are very difficult to sample, as they contain coarse lumps of metal and cannot be crushed to render them uniform. The best procedure is to sample down as usual and to fuse, under cyanide, as large a quantity as can be handled. A metal button or ingot is thus obtained which is sampled and assayed in the usual manner.

A preliminary examination should be carried out on the coarse or uncrushed ore, in order to identify as many of the mineral constituents as possible. For fusion assays this will enable the assayer to form a rough estimate of the gangue minerals, so that suitable quantities of reagents may be introduced into the furnace charge. For wet assaying this examination will suggest the presence of minerals which might cause interference in certain methods of assay, and will enable the assayer to select the most suitable procedure. When the material is received in the crushed condition it may be examined with a lens or under a microscope.

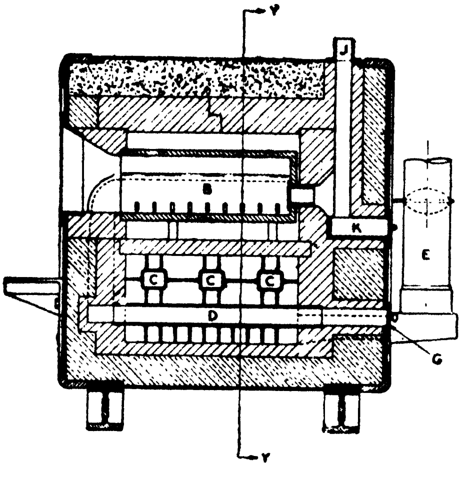
A concentration test is made in a miner's pan (a flat-bottomed, sheet-iron pan with sloping sides) or on a vanning shovel, but any basin or pan can be applied to the purpose. The ore is coarsely crushed, to liberate the mineral from the gangue, and a suitable weight is stirred and shaken with water in the pan, the lighter material being poured off into a basin. More water is added, and a further quantity of the gangue is washed off by a jerky, circular motion, this procedure being repeated until a reasonably clean concentrate of the heavy minerals is obtained. On the vanning shovel, the coarsely crushed ore is mixed with water by a vigorous circular motion. The lighter material is poured off, and the process is repeated until only the heavier minerals remain. A smaller quantity of water is then added, and the mixture is thrown forward, up the shovel, by a series of jerking movements. The heavier minerals cling to the surface and are separated from the lighter ones, which are washed back by the water. The tailings from either of these processes may be collected and retreated, and the concentrate, if coarse, should be rubbed down with a hammer and rewashed. The concentrate is weighed, examined under a lens, and may then be assayed by any suitable method. The pan is normally employed for the examination of gold ores, and the vanning shovel for tin ores, but any ore which contains heavy minerals associated with a light gangue can be treated by either method.

The *furnaces* used by assayers are the muffle furnace and the wind or crucible furnace. The former consists of a small oven or muffle made of fireclay, which is supported in the furnace in such a way that it is heated externally by the burning fuel. The front of the muffle is open to the atmosphere but can be closed, when necessary, by a firebrick door. Holes may be left in this door so that air can pass into the muffle, and a draught may be induced by opening a damper into a small flue connected to a hole at the back of the muffle. The fuel may be coke, oil, or gas, and burns in the combustion chamber surrounding the muffle. The furnace walls are of firebrick bound with iron plates, and may be covered with insulating material to check radiation. A new type of gas muffle furnace is illustrated in Figs. 1 and 2. Gas from the burners (A) passes up, over, and under the muffle (B), and thence across the outside of the recuperators (C and D) to the exit flue (E). The preheated air from (C) passes to the burner (A), and that from (D) enters the muffle by the passages (K) and passes out to the flue (J). The heat of combustion of the gas is thus better utilised, and there is a corresponding reduction in fuel consumption, accompanied by an increase in efficiency. A muffle, being full of heated air, has a strongly oxidising atmosphere, and is used for oxidising fusions and reactions such as roasting, scorification and cupellation. A second muffle furnace is usually reserved for the ignition of the precipitates and residues obtained in wet assaying. A crucible furnace (Fig. 3) consists of a firebox (A) with a flue (B) at the back, and a movable firebrick cover. The fuel may be coke, oil or gas. When coke is used the crucible is embedded in the fuel. Oil or gas is injected tangentially at the bottom of the furnace, the crucible being surrounded by the rotating and burning fuel. In either case the furnace has a reducing atmosphere and is particularly adapted to reducing fusions.



SECTION YY

FIG. 1.



SECTION XX

FIG. 2.

Crucibles are usually made of fireclay, but wrought-iron crucibles are frequently used for the assay of lead concentrates. Crucibles in which metals and alloys are melted are usually made of various graphite mixtures and other refractories. These crucibles are of many sizes and shapes, and are used in the wind furnace.

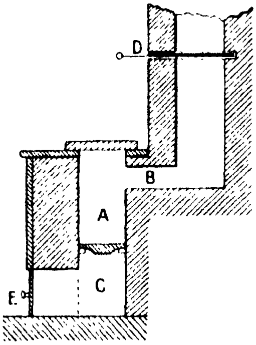


FIG. 3.

In America reducing fusions are carried out in large muffle furnaces, using a smaller type of vessel known as a "Colorado" crucible. *Roasting dishes* and *scorifiers* are also made of fireclay. They are flat, saucer-shaped dishes which expose a large surface to the atmosphere, giving rapid oxidation. They are used in the muffle furnace. *Cupels* are small, shallow cups made of bone-ash or, more commonly, of compressed magnesia, or of some similar absorbent material. They are required in the assay of the precious metals, and are used in the muffle furnace.

The *reagents* employed in fire assaying are of three types: oxidising agents, reducing agents, and fluxes. Generally speaking, an ore consists of a heavy metal, or compounds of a heavy metal (the mineral), associated with various earthy materials such as limestone, silicates, quartz, etc. (the gangue). The object of the assay is to reduce the valuable constituent to the metallic form and to incorporate the remainder of the ore in a fusible slag, through which the metallic particles can sink and collect in the form of a button. Sometimes a matte or regulus (sulphides of the heavy metals) or a speise (arsenides of these metals) will form a separate layer between the metal and the slag. As these compounds are objectionable, reagents must be added to prevent their formation. The reducing agents in common use are carbon (charcoal powder), flour, starch, argol (crude potassium hydrogen tartrate) or similar materials. One part of carbon is approximately equivalent to two parts of flour or five parts of argol, and a larger quantity of these reagents will be required. In the fusion of base metal concentrates, such as galena, where intimate contact is required between the reducing agent and a large quantity of the metallic mineral, the less powerful reagents are preferable owing to the larger amount used. Argol also has a fluxing value, as it decomposes, when heated, forming potassium oxide. Metallic iron, in the form of nails or hoop iron, is used as a desulphurising agent, as it unites with the sulphur and passes into the slag as ferrous sulphide. Potassium cyanide is used in certain fusions (principally for tin concentrates) and acts both as a reducing agent and as a flux. In certain cases its reducing power is increased by the addition of a little charcoal, and if the ore is highly basic a little borax may be added. The chief oxidising agents are hot air (in the muffle furnace), litharge or red lead, and nitre, and they are mainly used for the oxidation of sulphur and antimony. In the processes of scorification and cupellation, the hot air of the muffle furnace is used for the oxidation of metallic lead. Fluxes are of three kinds, acid, basic and neutral. The chief acid flux is borax, sodium biborate, which forms fusible borates with the oxides of the heavy metals and earthy bases. Crystallised borax swells on heating, giving up its combined water, and this swelling may cause loss if the crucible is too full. Borax which has been previously fused and crushed, called glass borax, is frequently used to overcome this objection. Clean crushed quartz and flint glass are also suitable for use as acid fluxes, and sand is sometimes added to a charge to protect the crucible from the corrosive action of basic oxides. The chief basic flux is sodium carbonate, which forms fusible mixtures with silica, alumina, zinc oxide and tin oxide. It also acts, to a certain extent, as a desulphuriser, converting pyrites into a mixture of the sulphides of iron and sodium. These sulphides pass into the slag without forming a regulus. Sodium bicarbonate acts similarly, but has the disadvantage of swelling more violently when heated. Other basic fluxes are lime, and a mixture of carbon and hematite to form ferrous oxide, but these are less frequently employed. Fluorspar, the neutral flux, is used for thinning slags which contain highly refractory minerals, such as apatite. Salt, another neutral material, is sometimes used as a cover to decrease surface tension and so to avoid loss by bubbling or "boiling."

The *balances and weights* do not differ from those used in chemical analysis, except in the case of those employed for the assay of gold and silver. The quantity of these metals is reported in troy pennyweights or ounces per ton (avoirdupois) of ore. The unit weight of ore taken for assay contains as many milligrams as there are troy ounces in a ton (32,666 in a ton of 2,240 lb., and 29,166 in a ton of 2,000 lb.). This weight of 32·67 g. is called a long assay ton (or A.T.), and boxes of weights made up of assay tons and decimals are in common use. The silver extracted from the ore sample is weighed in milligrams, this weight giving the ounces per ton without calculation. In the case of gold ores it is usual to treat 2 A.T., and the gold is weighed in tenths of a milligram, thus giving the pennyweights per ton. In the assay of gold bullion the special weights commonly range from "1,000" downwards, where 1,000=0·5 g., or some other convenient unit. Calculation is thus eliminated and the chance of error is much diminished. In the Indian Mint method for the assay of silver by precipitation as silver chloride (p. 529), a special series of weights is used. 25 parts of the chloride contain 18·815 parts of silver. 18·815 grains of the alloy are weighed for assay, and the resulting chloride is weighed with a series of weights, the largest of which is marked 1,000 and is equal to 25 grains. The fineness of the alloy is then read from the weights balancing the chloride. A similar series can, of course, be arranged for any particular purpose.

The balances used for weighing gold and silver in bullion assays are light and delicate, taking about 2 g. as a maximum load, and turning with one hundredth of a milligram. One division of the ivory scale is usually equal to 0·05 mg. Balances used for weighing the gold from ore assays are still more delicate, taking 1 g. or less as maximum load, and turning with one-hundredth or even one-fivehundredth of a milligram. Milligram and half-milligram riders are used, but the final reading is based on the deflection of the pointer from the zero position on the ivory scale. These balances usually have short beams of 6 in., 4 in., or even 8 cm. in length, so that they are rapid in action despite their sensitiveness. In quantitative blow-pipe work and in the assay of low-grade ores and tailings, it is possible to dispense with a delicate balance, using an ivory scale (Plattner's scale), by which the diameter of the almost spherical bead of metal is measured. This principle has been extended to the measurement of very minute beads under the microscope by means of a micrometer eyepiece. In this way L. Wagoner (Trans. Amer. Inst. Min. Eng. 1901, **31**, 798) obtained a close approximation to the weight of beads of silver of 0·02 mm. in diameter, which weighed about 0·0004 mg. The method assumes that the beads are of pure metal, or that the gold in the material under examination is in constant proportion to the silver.

The above summary refers to the requirements of a laboratory equipped for fire assaying. For wet assays the apparatus and reagents are those of the ordinary analytical laboratory (*v.* Chemical Analysis). Chainomatic balances are convenient for determinations which involve a change in weight (*e.g.* moisture, ignition loss, etc.). Electric tube furnaces are now in general use for combustion work (*e.g.* the determination of carbon in steels), and electrically heated muffles are advantageous for ignition work, as the temperature is easily controlled and there is no danger of the introduction of objectionable fumes into the sample.

The methods described in the following pages are in common use in assay laboratories. It should be understood that few assay methods can be applied indiscriminately to all classes of metallurgical materials. Each class requires separate consideration, and the method adopted is generally based on the particular method of separation which is best suited to the material under examination. When separation can be avoided, direct determinations are always made.

Aluminium.—In the examination of the ores of aluminium, the most important consideration is the quantity and nature of the impurities present. A complete analysis of the ore is, therefore, required, and the usual group separation is employed. The ore is rendered soluble by fusion with potassium bisulphate or with alkalis, and silica is removed. The iron group is first separated with ammonia and is redissolved and reprecipitated by the basic acetate method. Iron is determined after re-solution of this precipitate. Phosphorus and titania are determined on separate samples, and alumina is found by difference. The alumina and titania may be separated and weighed together as phosphates if preferred, the alumina being found by deducting the titania present (J. T. Pattison, "Manufacture of Aluminium," Spon, 1918, 42).

Aluminium in metallic aluminium and in high aluminium alloys is best estimated by difference after the determination of the other constituents and impurities. These, with the exception of zinc, silicon and chromium (when present), are best separated with caustic soda, bromine and a little sodium carbonate. Small quantities of aluminium in alloys such as brasses, steels, etc., are usually determined by the phosphate method after separation of interfering constituents (J. T. Pattison, *ibid.* 89, 92).

Antimony.—This metal is conveniently determined in sulphide ores by attacking the finely ground sample with hot concentrated sulphuric acid, diluting, adding hydrochloric acid, and titrating the cold solution with potassium permanganate. Arsenic interferes, the titration giving the combined equivalents of the two metals. Tin, lead, bismuth and copper in ordinary amounts do not interfere, and a considerable percentage of iron affects the result to only a slight extent. This method may also be applied to many alloys (Clennell, Mining Mag. 1931, **45**, 151). Ores may also be attacked by fusion with sulphur and sodium carbonate. The alkaline sulpho-compounds are dissolved in water, and the sulphides are reprecipitated with acid. The antimony may be separated from the insoluble sulphide of arsenic by digestion with 2 : 1 hydrochloric acid and reprecipitated from the diluted filtrate with sulphuretted hydrogen. The metal is conveniently determined in a tartrate solution rendered alkaline with sodium bicarbonate by titration with iodine.

A method which is suitable for many alloys, and in particular for the determination of antimony in hard lead, is the *bromate method.* The metal sample is dissolved in hydrochloric acid and bromine water. The bromine is then expelled by evaporation to small bulk, and more acid and a saturated solution of sodium sulphite are added. Further evaporation expels arsenic and the excess of sulphur dioxide. If much arsenic is present, another evaporation is advisable. The hot solution is then titrated with potassium bromate, four drops of methyl orange being added as indicator just before the conclusion of the titration. If the approximate composition of the alloy is not known, a portion of the solution should be set aside and added, with more indicator, when the titration of the first portion has been concluded (Scott, "Chemical Methods for Analysis of Metallurgical Products," Van Nostrand, 1928, 24).

Arsenic.—In Pearce's method, the ore is fused with a mixture of equal parts of sodium carbonate and nitre. The alkaline arsenates are dissolved in water, filtered, and precipitated in neutral solution with silver nitrate. The filtered silver arsenate is dissolved in nitric acid, and the silver is determined by Volhard's thiocyanate method, whence the arsenic is calculated (Low, "Technical Methods of Ore Analysis," Chapman and Hall, 1927, 37). A convenient method for the simultaneous determination of arsenic and antimony is, briefly, as follows. The finely crushed sample is mixed with potassium bisulphate in a pyrex glass flask and some sulphuric acid and a small piece of filter paper are added. The mixture is heated to oxidise all carbon and to expel the excess of acid, and is finally brought to fusion. The melt is cooled over the sides of the flask and is leached out with 2 : 1 hydrochloric acid. The arsenic is then precipitated with sulphuretted hydrogen and filtered, the antimony being recovered from the filtrate. The arsenic is determined by solution in sulphuric acid and iodometric titration (Low, *ibid.* 24). Small quantities of arsenic are best determined by an evolution method. Ores are first attacked with nitric acid to destroy sulphides, and are then fumed with sulphuric acid. The solution is distilled with hydrochloric acid and ferrous or cuprous chloride, the arsenious chloride being collected in cold water. The determination is concluded either iodometrically or gravimetrically (Scott, "Chemical Methods for Analysis of Metallurgical Products," 101).

Bismuth is usually separated from other metals as oxychloride, this compound being converted to the basic carbonate by double precipitation with ammonium carbonate. The residue is weighed, after ignition, as oxide. Small quantities of bismuth are determined colorimetrically. Interfering metals, such as copper, iron, etc., are separated, and the bismuth is measured by the depth of colour given with potassium iodide in nearly neutral solution. A small amount of sulphurous acid is used to remove any colour due to iodine (Beringer, "Assaying," Griffin, 1921, 223).

Chromium in chrome iron ore is determined by a volumetric method based on the oxidation of ferrous iron by solutions of chromates. The chromium is oxidised and rendered soluble by fusion with sodium peroxide. The cooled melt is leached out with water and acidified with sulphuric acid. The peroxide is destroyed and the manganese oxide removed, and the chromium is reduced by the addition of a known quantity of a ferrous salt. The excess of the latter is found by titration with potassium permanganate or dichromate. Small quantities of chromium are determined gravimetrically as lead chromate, or by iodometric titration of this chromate. Colorimetric methods are based on the colour of dichromate solutions, and on the colour given by these solutions with diphenyl carbazide (Scott, "Chemical Methods for Analysis of Metallurgical Products," 228).

Chromium in steel is determined volumetrically after oxidation with bismuthate, persulphate, or permanganate. The oxidised manganese compounds are removed or destroyed, and the chromium is determined by back-titration with ferrous sulphate and permanganate (Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel," Chapman and Hall, 1931, 288).

Cobalt is generally determined by precipitation with nitroso-β-naphthol in hydrochloric acid solution, after separation of all metals which would interfere. The method of separation selected depends upon the composition of the material under examination. The usual group separation is satisfactory provided the metals of the iron group are precipitated as basic acetates, and the removal of heavy metals with an excess of zinc oxide emulsion, followed by filtration of an aliquot portion of the solution, is common. In the presence of nickel the two metals are frequently determined together by the electrolytic, gravimetric, or volumetric (cyanide) method, and the nickel is determined separately by the dimethyl glyoxime precipitation, the cobalt being found by difference (Scott, "Chemical Methods for Analysis of Metallurgical Products," 234).

Cobalt in steel is determined by the nitroso-β-naphthol method (United Steel Co.'s "Standard Methods of Analysis," 1933, 23). Small quantities of cobalt are determined colorimetrically by matching the blue colour of a boiling hydrochloric acid solution with a standard. The colour of ferric chloride is removed with stannous chloride (Keffer, "Methods in Non-Ferrous Metallic Analysis," McGraw-Hill, 1928, 94).

Copper in ores and concentrates is usually determined by the *iodide* method. The sample is attacked with mixed acids, and is fumed with sulphuric acid to precipitate lead and to remove nitric acid. The copper is then separated either as sulphide with sulphuretted hydrogen or thiosulphate, as thiocyanate after reduction with sulphur dioxide, or as metallic copper by precipitation on aluminium or zinc The separated copper is redissolved in nitric acid, bromine is added, and the mixture is boiled to prevent the interference of arsenic and antimony. The acid is neutralised with a minimum of ammonia, acidified with acetic acid, and again boiled to remove any remaining oxidising compounds. When cold, an excess of potassium iodide is added, and the liberated iodine is titrated as usual with thiosulphate. It is essential to remove all nitrous fumes by boiling or by the addition of urea. Ferric acetate interferes, and iron salts must be separated. Their effect may be inhibited by the addition of phosphoric acid. Sodium carbonate may be used for the neutralisation in place of ammonia, or the mineral acid may be destroyed by the addition of an excess of zinc acetate. To avoid the use of much costly potassium iodide, Moir proposed (J. Chem. Met. Soc. S. Africa, 1917, **18**, 133) adding a slight excess of sodium thiosulphate to the faintly acid solution of cupric acetate, and to titrate back with iodine, of which only a small quantity is required. The iodide method gives very accurate results and can be used, without separation, for the assay of alloys of copper with zinc, aluminium, nickel or tin, provided the tin does not exceed about 30% (Low, "Technical Methods of Ore Analysis," 78).

In the *cyanide* method the ore is dissolved in the appropriate acids, an excess of ammonia is added, and the solution is diluted to some convenient bulk, such as 200 ml., and is titrated with potassium cyanide to a colourless end-point. The results are affected by time, temperature, degree of dilution, and by the amounts of ammonia and ammonium salts. These conditions must, therefore, be kept constant. Zinc, silver, nickel and cobalt also react with the cyanide, and in their presence the copper must be separated. The hydroxides of iron and aluminium render the titration tedious, as the precipitate must be settled before the colour of the solution can be seen. A similar quantity of these metals should be added to the check samples unless the copper is separated. The method is rapid, even when a separation is made, and the results are reasonably accurate. It is largely used for control work where comparative results are required. (Beringer, "Assaying," 194).

Low-grade ores, tailings, slags, etc., are assayed by the colorimetric method. The sample is dissolved as usual, and the copper is separated if strict accuracy is required. The copper is redissolved in nitric acid, rendered ammoniacal, and the colour is matched by adding a standard solution of copper to a similar bulk of acid and ammonia. Copper up to 5% may be determined by this method, but greater accuracy is obtained with smaller proportions (Beringer, "Assaying," 203).

The *electrolytic* assay is particularly suited to the analysis of metallic copper and copper alloys, but it may be applied to complex ores and other materials by giving a suitable preliminary separation. The copper solution is adjusted to contain about 5% of nitric, sulphuric, or a mixture of both acids, and is electrolysed with a current of 0·5 amperes per sq. dcm. of cathode surface, at 2·1 volts. The electrodes are a spiral platinum anode and a platinum cone or gauze cathode. The electrolysis is continued for 16 or 17 hours, after which the electrodes are washed with water, and the cathode is removed, dried, and weighed. Any small quantity of copper left in the solution is determined by the colorimetric method, but the deposition should be complete. Silver, mercury, bismuth, arsenic, and antimony interfere with the process and should be removed. Silver may be precipitated as chloride and filtered from the solution, but all chlorides must then be removed, or some platinum will dissolve from the anode and deposit with the copper. Mercury may be removed as sulphide, which is insoluble in nitric acid. Bismuth, arsenic and antimony are not completely deposited, and the error due to small quantities of them may be overcome by redissolving the deposit in nitric acid, adjusting the acidity to 1% of concentrated nitric acid, adding 5% of ammonium nitrate, and repeating the electrolysis. When using a sulphuric acid solution some lead may accompany the copper, but from nitric acid solutions it is oxidised and deposits on the anode as lead peroxide, in which form it may be weighed.

By increasing the current density to 10 to 12 amperes per sq. dcm. and agitating the solution, the time required for the deposition may be reduced to a few minutes. The interference of other metals is somewhat increased by this treatment, and for accurate results the electrolysis should be repeated as described above, or a preliminary separation may be made. The solution is agitated by the use of a stirrer or by the rotation of one of the electrodes, and the latter are preferably made of platinum gauze to facilitate circulation of the liquid.

Commercial copper varies considerably in composition. Electrolytic copper is nearly pure, but lower grades of metal may have 2 or 3% of impurities. Arsenic, lead, nickel, oxygen and phosphorus are the chief impurities, but antimony, bismuth, cobalt, gold, iron, selenium, silver, sulphur and tellurium may have to be determined. Arsenic is determined by evaporation of $AsCl_3$ from an acid ferric chloride solution. Antimony and phosphorus are separated as their iron salts in a basic acetate precipitate. Gold is left undissolved by solution of the copper in nitric acid, and is collected for filtration in a precipitate of lead sulphate. Silver is precipitated as chloride or, better, as bromide from a nitric solution, and is collected in a precipitate of lead sulphate or chloride. In both these cases the determination is concluded by scorification, cupellation and parting. More accurate results for gold are obtained by direct scorification with silica and lead, the treatment being repeated until all copper is removed. The lead button is then cupelled as usual. Nickel is determined by precipitation with dimethylglyoxime, preferably after electrolytic separation of the copper. Lead and manganese are indicated by the dark deposit on the anode in the electrolytic assay for copper; the lead is determined as sulphate or chromate, and the manganese is oxidised to permanganate and measured either colorimetrically or by titration. Bismuth is first separated as a basic carbonate by the addition of a little ferric chloride and an excess of sodium carbonate. This is redissolved in acid and rendered alkaline with soda and sodium tartrate. Potassium cyanide is added, and bismuth and lead are precipitated as sulphides. The bismuth is finally determined by the colorimetric method. Selenium and tellurium are collected in a ferric hydroxide precipitate, separated with sulphuretted hydrogen in an alkaline tartrate solution, and subsequently precipitated from a hydrochloric acid solution with sulphurous acid. The selenium is then separated from the tellurium by digestion with potassium cyanide. Oxygen is determined by heating the sample in a current of hydrogen, water and hydrogen sulphide being liberated. Sulphur is precipitated as barium sulphate after removal of silver chloride.

Copper alloys are dissolved in nitric acid for the separation of tin with any phosphorus, the latter being held in the stannic acid residue after evaporation. Tin is determined by dissolving this residue in boiling sulphuric acid, reducing, and titrating with iodine, or by direct weighing if the residue is very small. Phosphorus is rendered water-soluble by fusing the residue with potassium cyanide, and, after separation of impurities, is precipitated with magnesia mixture. The original filtrate is evaporated with sulphuric acid for the removal of lead, and the copper is determined by electrolysis. The solution is then available for the determination of other constituents and impurities by the usual methods.

Gold is generally found in nature in the metallic state, either as grains or scales in alluvial deposits, or finely disseminated through the gangue matter in veins. It is frequently associated with the minerals of the base metals, such as iron and copper pyrites, zinc blende, etc., but the only native compounds of gold are the tellurides. Other materials with which the assayer must deal are tailings and residues, copper bottoms, pig lead, unrefined bullion, refined (fine) gold and commercial alloys. The assay of gold ores and alloys is made with great exactness, owing to the high value of the metal.

A *panning assay* or *concentration test* has been described on p. 519. The concentrates may consist of "black sand" (oxides of iron and titanium, etc.), base metal sulphides and arsenides, and, sometimes, grains of platinum. Free gold may be visible, and is collected by grinding in a mortar with mercury, panning out the amalgam, and removing the mercury by distillation or by solution in nitric acid. In the former case the gold must be parted from the silver as described on p. 525. About 60 to 90% of the gold present is usually recovered in this way.

Gold ores, tailings, residues, etc., are assayed by the crucible fusion method. Very rich materials may, however, be conveniently handled by the method of scorification described under silver (p. 529). In the crucible fusion method the sample, crushed to 80-mesh or finer, is mixed with litharge or red lead, charcoal or other reducing agent, and the necessary fluxes, and is fused in a crucible furnace. In the "Colorado" assay, small charges are fused in small crucibles in a muffle furnace. The weight of ore taken varies with the probable gold content from ½ A.T. to as much as 10 A.T., which would be fused in several charges, the gold being collected into one button by repeated scorification. The fluxes and treatment vary with the nature of the gangue, and the following typical charges are subject to very considerable modification.

	A. Siliceous (with little pyrites).	B. Basic (oxidised ore).	C. Pyritic.
Ore	1 A.T.	1 A.T.	1 A.T.
Litharge or red lead	40 g.	40 g.	40–75 g.
Charcoal	1·5 g.	2–3 g.	0–1 g.
Sodium carbonate .	40 g.	25 g.	25 g.
Borax	5 g.	15 g.	15 g.

Sand may be added to B and C, if advisable, to protect the crucible from corrosion by the basic oxides. 5 g. of the borax is set aside and added to the charge as a cover. The remainder of the charge is well mixed and transferred to the crucible, which should not be more than two-thirds full. A piece of hoop iron or two or three tenpenny nails are pushed into the mixture when sulphides are present. The crucible is heated gradually to the "fritting" temperature at which the charge becomes pasty, is held at that temperature for about ten minutes, and is then further heated to tranquil fusion. The total heating period is about 40 to 50 minutes. The pot is then removed and the charge is poured into a warm, dry, conical iron mould. When cool, the lead button is detached from the slag by hammering. It should weigh about 25 to 30 g., and if it is too small a fresh charge is prepared which contains more charcoal. At the same time any desirable changes are made in the proportions of the fluxes. If the lead is too heavy, or is hard and brittle owing to the presence of impurities, it is scorified, sometimes with the addition of more lead, before cupellation. The slag will carry a little silver, and will also contain a small quantity of gold if the charge has been fused under oxidising conditions. For this reason the oxide of lead should be completely reduced so that none passes into the slag, and the more readily oxidised metals, such as iron, should be brought to the lower state of oxidation. Metals which are easily reduced, such as copper, antimony, etc., will then mostly pass into the lead button. This is a disadvantage, as they will increase the normal cupellation losses. Copper and nickel may be removed from the ore before fusion by a preliminary treatment with nitric acid. Small quantities of copper may be carried into the slag by fusing under oxidising conditions with an excess of litharge, but the slag must be "cleaned" by a second fusion, with the reduction of more lead. A similar method of fluxing is used for telluride ores, the litharge slag preventing the tellurium from entering the lead button. Arsenical ores are roasted with carbon to volatilise the arsenic, and antimonial ores are fused with sufficient nitre to oxidise the antimony and carry it into the slag as an antimoniate. Sulphides are roasted before fusion if they are unsuitable for direct treatment.

The lead button, hammered free from slag, is placed on a hot cupel in the muffle furnace. The lead melts and oxidises, the molten litharge being absorbed into the cupel. The gold and silver do not oxidise and are finally left as a small bead, or "prill," on the surface of the cupel. If this bead is large and contains much silver, it must be cooled gradually to prevent loss by "spitting" when it solidifies. The prill is cleaned, flattened by hammering, and weighed. The silver is then removed by "parting" in boiling nitric acid. The removal of silver is not complete if too little of that metal is present in the bead, and it may be necessary to melt more silver with it, the actual proportion required depending upon the weight of gold present, thus :

Weight of gold.	Silver required for parting.
10 milligrams.	40 milligrams.
1 ,,	6 ,,
0·2 ,,	2 ,,

A small excess of silver is permissible, but if too much is present the gold will break into a very fine powder which is difficult to wash without loss. By dropping the flattened bead into boiling nitric acid of sp.gr. 1·2, the powdering of the gold is reduced to a minimum. The parted gold is washed free from silver nitrate, and is rendered coherent for weighing by annealing at a red heat. The silver is found from the loss in weight. The reagents should be tested for gold and silver by running blank fusions.

During cupellation some silver and a little gold are carried into the cupel with the litharge, especially if copper, nickel, tellurium, etc., are present. These values are recovered by fusing the crushed cupel with litharge, charcoal, sodium carbonate, borax, and fluorspar, and cupelling the button of lead. The slag from the crucible fusion is often added to this charge to recover any values contained in it.

Gold bullion and alloys.—The assay piece is cut and filed to correspond to the standard weight marked "1,000." As already explained (p. 521), this weight varies in different offices, but is usually 0·5 g. A piece of pure assay silver, 2½ times the weight of the gold believed to be present, is then added, and the whole is wrapped in sheet lead. The weight of the lead depends mainly on the amount of copper present and varies from 8 to 32 times the weight of the assay piece. When dealing with alloys of unknown composition, the approximate value is determined by a preliminary assay, or by means of the touchstone (p. 526). The lead packets are placed on cupels which have been raised to a bright red heat in a muffle. In about 10 to 20 minutes iridescent bands of colour are seen to pass rapidly over the surface, and the disappearance of the incandescent litharge makes the buttons appear cooler. A few minutes later the muffle is closed to allow the buttons to set without loss by spitting. This danger is avoided when copper is present, and the cupels may be withdrawn while the buttons are still molten. At the Royal Mint a charge consists of 72 assay pieces. These are charged simultaneously by means of a divided metal tray with a sliding bottom, and they are withdrawn by means of a tray of refractory material on which the cupels stand. The buttons are brushed clean, flattened on an anvil, annealed, and reduced to a thickness of about 0·2 mm. by passage through a small pair of "flatting" rolls. The "fillets" are annealed again, and coiled into a spiral or "cornet" between the finger and thumb. The cornets are parted either in glass parting flasks or in a platinum boiling apparatus by boiling in nitric acid of sp.gr. 1·2 for 2 or 3 minutes after the red fumes have disappeared. The acid is poured off and, after two washes with boiling water, a further treatment is given with somewhat stronger acid. The acid must be free from chlorine, etc., or some gold will be dissolved. After further washing, each cornet is transferred to a porous crucible or "annealing cup," by filling the flask with water, placing the cup over the mouth, and inverting the flask. The flask is then removed gently without agitating the water. The gold is dried, annealed, and weighed. The cornets will not break up unless the weight of silver present is more than three times the weight of the gold; and if the composition of the bullion is known sufficiently closely to avoid risk of breakage of the cornets, the latter may be parted in batches in small platinum cups held in a platinum tray. The whole tray is immersed in boiling acid, washed, and retreated in a second acid. At the Royal Mint the cornets are treated in this way, being boiled twice for 30 minutes in fresh acid of sp.gr. 1·23. In each batch of samples two or more check assays are made on pure gold to which the appropriate quantity of silver and base metal is added. In this way the " surcharge " is determined, this being a correction for the losses of gold and the small quantity of silver retained. Check assays are of little value when the assays are parted in separate flasks (Rose, " Metallurgy of Gold," 6th ed., Griffin, 1915, 525–555).

An interesting method employed at the Birmingham Assay Office is to heat the alloy in a current of steam for 5–10 minutes with a weight of copper amounting to 2 or 2¼ times the weight of gold present. The temperature is a little above the melting-point of copper. The resulting bead is flattened and parted in nitric acid. Any zinc is volatilised, and other impurities form an oxidised crust which is removed during hammering. Surcharges are always positive, as there is no cupellation loss and some copper is retained. Excellent results are obtained, even with low-grade bullion (Westwood, J. Inst. Metals, 1922, **27**, 307).

A volumetric method has been devised by W. B. Pollard. The sample is dissolved in aqua regia, and most of the gold is precipitated by titration with sodium arsenite in the presence of urea, potassium bromide, mercuric chloride, and mercuric iodide. A special *o*-tolidine indicator solution is then added, and the yellow colour is titrated out with a solution of quinol. Palladium is the only metal likely to give serious interference (Trans. Inst. Min. and Met. 1932, **41**, 434).

Alloys of gold and silver.—If these contain sufficient silver and base metals, they may be parted direct in nitric acid, the dissolved silver being precipitated with hydrochloric acid or salt and weighed as chloride. If the silver is insufficient for this treatment, the alloy is cupelled with lead to remove base metals, and is then again cupelled with sufficient silver to form a parting alloy. After parting, the silver is found by difference. The alloy may also be melted under potassium cyanide with sufficient cadmium to form a parting alloy, and, after parting, the silver may be determined volumetrically or gravimetrically.

Assay by touchstone.—In this ancient method, the sample is scraped on a black, acid-proof, abrading surface, known as the " touchstone." The streak is treated with nitric acid, and its colour is compared with that of streaks similarly produced by a series of alloys of known composition, called " touchneedles."

Iridium occurs alloyed with platinum, and so finds its way into gold bullion. During cupellation it sinks to the bottom of the bead and can be seen, after rolling, in the form of black scales on the outside of the cornet. It may be estimated by dissolving away the gold in aqua regia, the iridium remaining insoluble.

Iron ores are assayed volumetrically, by titration with potassium dichromate or potassium permanganate. The ores, being oxides or carbonates, are usually soluble in hydrochloric acid. Solution may be assisted by small additions of stannous chloride or, if any pyrites is present, nitric acid. The latter must be removed before reduction, either by evaporation to fumes with sulphuric acid or by precipitation of the iron with ammonia, filtration and re-solution in hydrochloric acid. Insoluble (*e.g.* titaniferous) ores are fused with potassium bisulphate, the cooled melt being dissolved in acid. Reduction is effected by one of the three following methods: (*a*) Stannous chloride is added, drop by drop, to the hot concentrated hydrochloric acid solution, until the yellow colour is discharged, two drops being given in excess. After cooling, the excess of stannous chloride is oxidised by an addition of mercuric chloride. (*b*) The dilute acid solution is boiled gently with metallic zinc until reduction is complete and the excess of zinc is removed by filtration through a glass-wool pad. (*c*) The solution is nearly neutralised with ammonia and crystals of sodium sulphite are added. The mixture is warmed until reduction is complete and the excess of sodium sulphite is destroyed by boiling with acid until all sulphur dioxide has been removed. This tedious method is only employed in the presence of titanium.

The reduced chloride solution is titrated, cold, with potassium dichromate, using potassium ferricyanide as an external indicator, or diphenylamine as an internal indicator. Titration with potassium permanganate must be carried out in a sulphuric acid solution free from chlorides. The hydrochloric acid solution of the ore is, therefore, evaporated with sulphuric acid, and reduction cannot be effected with stannous chloride. This objection is overcome in the Reinhardt-Zimmermann method, in which a special solution of manganous sulphate and phosphoric acid is added just before titration. This serves to retain the chlorine liberated by the permanganate, and decolorises the yellow ferric chloride by the formation of ferric phosphate. A definite but somewhat fugitive end-point is obtained.

The ferrous iron in an ore is determined by solution in hydrochloric acid in a neutral atmosphere. Ferric iron is found by difference, or the sample is dissolved as in the last case and is titrated, hot, with a standard solution of stannous chloride, the yellow colour of the ferric chloride acting as indicator.

In the examination of iron ores the determination of impurities such as sulphur, phosphorus, arsenic and manganese, which would affect the quality of the resulting pig iron, is of great importance. The methods used are similar to those employed in the analysis of steel.

Analysis of iron and steel.—The elements to be determined are carbon (graphitic, combined, and total carbon), silicon, sulphur, phosphorus, manganese and arsenic. In alloy steels, chromium, nickel, cobalt, tungsten, molybdenum, vanadium, etc., may also be required. Total carbon is generally determined by direct combustion, with or without the use of admixtures, such as red lead or bismuth oxide, which ensure the complete oxidation of the carbon. The carbon dioxide produced is measured gravimetrically or gasometrically (Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel," 154). The iron may also be dissolved in cupric potassium chloride, leaving the carbon insoluble. This is filtered on asbestos, washed, dried, and burned as usual. Graphite is separated by dissolving the iron and combined carbon in nitric acid of sp.gr. 1·2, filtering, and burning. Combined carbon is best found by difference, but may be estimated by comparison of the colour of a nitric acid solution of the sample with that of a solution of a similar steel of known composition. Silicon is weighed as silica, after solution of the metal in acids. Sulphur is determined gravimetrically as barium sulphate, after solution in an oxidising mixture of acids and removal of silica. For rapid works analysis the sulphur is evolved as sulphuretted hydrogen, collected in cadmium acetate or sodium hydroxide, and titrated iodometrically. A variation of this method is to pass the evolved gases through a series of test-tubes containing known volumes of standard lead acetate solution. The percentage of sulphur is shown, without calculation, by the number of darkened tubes. Phosphorus is precipitated and weighed as ammonium phosphomolybdate or is converted to magnesium pyrophosphate. The former precipitate may be dissolved in standard alkali, the excess of which is titrated with acid. Manganese is precipitated with bromine and ammonia after a basic acetate separation of the iron, or is oxidised with lead peroxide, sodium bismuthate, or ammonium persulphate, and determined colorimetrically or by titration with sodium arsenite. Arsenic is found by evolution as arsenious chloride, followed by iodometric titration (Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel," Part II).

(For the determination of constituents of alloy steels, *see* under the appropriate headings, chromium, nickel, etc.)

Lead.—Although the fire assay is still used for concentrates in some localities, wet assay methods are generally preferred, and they must be used for low-grade materials. For dry assay the ore is crushed to 60-mesh and mixed with sodium carbonate, argol, and, if necessary, borax. Clay crucibles are frequently used, but galena is generally fused in an iron crucible, thereby avoiding the use of hoop iron. Borax is normally used as a cover, even when it is not required in the charge. The following charges are typical for rich concentrates :

	1. Galena.	2. Cerussite.	3. Pyromorphite.
	grams.	grams.	grams.
Ore.	30	30	30
Argol	3	6	6
Sodium carbonate	25	20	25
Borax	—	15	10

Hoop iron must be used for galena, unless the fusion is carried out in an iron crucible, and is advisable in each charge. A little fluorspar will help to render charge No. 3 more fluid, as it is liable to carry refractory phosphates. When clay crucibles are used the procedure is the same as for the fusion of gold ores, except that the charge should be run at the lowest possible temperature to avoid volatilisation and the formation of lead silicate. The iron crucible is first raised to a red heat and scraped clean. It is then cooled to a black heat and the charge is transferred to it, the borax or part of the soda being added as a cover. The charge is heated slowly and, when in tranquil fusion, is poured into a mould. When cold, the lead is hammered free from slag and weighed. The button should be soft and malleable. If hard or brittle, the presence of antimony, copper, etc., is indicated. Arsenic will form a speise which adheres to the upper surface of the button, and any gold and silver are collected into the lead. Pure concentrates will give results about 1 or 2% too low. Impure ores will usually give high results, and should be treated by wet methods.

For wet assays the ores are dissolved in hydrochloric acid, assisted, if necessary, by nitric acid. The lead may be determined gravimetrically as lead sulphate, or, more usually, volumetrically. In Alexander's method the solution of the ore is evaporated with sulphuric acid, diluted, boiled, cooled and filtered. The lead sulphate is dissolved in hot ammonium acetate, acidified with acetic acid, and titrated at the boiling-point with a standard solution of ammonium molybdate. Tannic acid, which gives an orange-yellow colour with the molybdate solution, is used as an external indicator. If much lime is present, it is better to separate the lead as sulphide and redissolve for titration (Low, "Technical Methods of Ore Analysis," 131). In the *chromate* method the lead sulphate is separated as before, dissolved in sodium acetate, and the lead is reprecipitated as chromate. This is dissolved in an acid solution of sodium chloride, the chromic acid is reduced with potassium iodide, and the liberated iodine is titrated with sodium thiosulphate (Low, *ibid.* 124).

Manganese occurs in pyrolusite as manganese dioxide, which is valuable for its oxidising properties. It is frequently necessary, therefore, to determine the "available manganese," which is the percentage of manganese dioxide. The total manganese content of ores, spiegeleisen, and ferromanganese is determined by Volhard's method. The ore or alloy is dissolved in nitro-hydrochloric acid and fumed with sulphuric acid. Iron is precipitated with excess of zinc oxide emulsion, and the mixture, or a filtered, aliquot portion of it, is titrated at the boiling-point with potassium permanganate to the appearance of a permanent pink colour. A ml. or so of glacial acetic acid is added to discharge the colour and coagulate the precipitate, and titration is continued, without further boiling, to the usual end-point. The bismuthate method is also applied to such materials by dissolving the sample and taking a small aliquot portion of the solution for oxidation with this reagent. The permanganic acid is titrated with ferrous sulphate. All chlorides must be removed from the solution (Low, *ibid.* 146, 148). Available manganese is determined by attacking the sample with hydrochloric acid and collecting the evolved chlorine in a solution of potassium iodide. The iodine, liberated by the chlorine, is titrated with sodium thiosulphate. Alternatively, the sample may be dissolved in sulphuric acid containing ferrous sulphate or oxalic acid, the excess of reducing agent being found by titration (Sutton, "Volumetric Analysis," Churchill, 1935, 286–289).

Mercury is normally determined by distillation, Rose's method being used for concentrates. A hard glass combustion tube is sealed at one end, and some magnesite powder is placed in it, followed by a layer of quicklime. The ore sample, which has been previously crushed in a mortar with an excess of quicklime, is then added and the mortar is cleaned with more lime which is passed into the tube. A cover of clean lime is added, and the charge is held in place with a loosely fitting plug of asbestos. The end of the tube is drawn out almost to a point, and is bent over at right angles. The tube is placed in a combustion furnace and tapped, to settle the charge and leave a clear passage for the gases. The exit tube dips below the surface of some water in a beaker. The tube is then heated, starting at the asbestos plug and finishing with the magnesite, the latter yielding enough carbon dioxide to sweep out the mercury vapour. Heating should occupy about 30 minutes. While the tube is still red hot, the narrow end is cut off and dropped into the beaker. The mercury is collected in the water, drained, and dried, first with blotting paper, and then in a desiccator, and is finally weighed (Beringer, "Assaying," 172). Low-grade ores are assayed by the Holloway-Eschka method. An ore sample, containing a maximum of 0·1 g. of mercury, is mixed with about ten times its weight of iron filings in a porcelain crucible, the rim of which has been ground level. A cover of filings is added, and a clean, weighed silver plate is placed over the crucible. This is cooled and held in close contact by a small water condenser. The crucible is supported in a hole in a sheet of asbestos board, and is slowly warmed until the bottom is just red hot. The mercury volatilises and amalgamates with the silver plate, which is dried and reweighed (Scott, "Chemical Methods for Analysis of Metallurgical Products," 384).

Molybdenum is most conveniently determined by precipitation as lead molybdate in an acetic acid solution containing a considerable excess of ammonium chloride and ammonium acetate. The precipitate may be ignited without any special precautions after the filter paper has been charred (Schoeller and Powell, "Analysis of Minerals and Ores of the Rarer Elements," Griffin, 1919, 163). In the presence of tungsten and vanadium, the molybdenum should be separated as sulphide in a tartaric acid solution (Hillebrand and Lundell, "Applied Inorganic Analysis," Chapman and Hall, 1929, 247).

Molybdenum in steel.—Tungsten, if present, is separated with the silica by dissolving in hydrochloric acid assisted by nitric acid, and evaporating just to dryness without baking. The residue is taken up in 20% hydrochloric acid, filtered, and poured into an excess of hot sodium hydroxide solution. An aliquot portion of the solution is separated by filtration, and the molybdenum is precipitated as lead molybdate (Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," 320).

Nickel is normally determined by precipitation with dimethylglyoxime. The sample taken should not contain more than one decigram of nickel or the precipitate will be too bulky for easy washing. Silica must be separated. In the case of insoluble sulph-arsenide ores, a potassium bisulphate fusion will dehydrate the silica and render the nickel soluble. Copper, if present in large quantity, should be separated, as it will contaminate the precipitate, necessitating re-solution and reprecipitation. Cobalt is held in solution by using an excess of the precipitant. Metals of the iron group are not precipitated in the presence of a sufficient quantity of ammonium citrate or tartrate, and the metals of the subsequent groups are held in solution by ammonium chloride. The precipitate may be dried and weighed as nickel dimethylglyoxime, or wrapped in wet filter paper, charred at a low temperature in a covered crucible, and then ignited to nickel oxide (Scott, "Technical Methods for Analysis of Metallurgical Products," 402).

A volumetric method depends upon the interference of nickel in the titration of cyanide with a standard solution of silver nitrate. The titration is carried out in a slightly ammoniacal solution, potassium iodide being added to form a silver-iodide indicator. The titration may be run in either direction. The cyanide is usually standardised against the silver nitrate, but a pure nickel salt may be used. Iron may be separated, but the addition of citric acid will overcome the interference of this metal. Copper, cobalt, and zinc must be removed, as they react in a similar manner. When dealing with complex ores, it is convenient to precipitate the nickel with dimethylglyoxime, filter, redissolve in nitric acid, and destroy the organic reagent by boiling with an oxidising agent, such as persulphate. The solution is then treated by the volumetric method (Sutton, "Volumetric Analysis," 278).

Nickel in steel is determined by either of the above methods, the latter being more common in routine analysis.

Platinum may be concentrated from alluvial deposits by panning. In the normal procedure of fire assaying, as described under gold (p. 524), the platinum is concentrated into the lead button with the gold and silver. The lead should be cupelled at a very high temperature, but the melting-point of the alloy rises as the lead is removed, and the prill may "freeze" before the whole of the lead is oxidised. This difficulty may be overcome by adding a sufficient excess of gold and silver to produce an alloy of a lower melting-point. The flattened bead is then treated by the process of double parting, as described below under alloys of gold and platinum. After parting in nitric acid, the platinum may be precipitated, with some silver, by adding sulphuretted hydrogen water. The sulphides are filtered, burned, cupelled, and parted again in sulphuric acid to recover the platinum. An alternative method is to dissolve the lead button in nitric acid, to filter off the residue of gold and platinum, and to dissolve it in aqua regia. The gold may then be precipitated with oxalic acid and the platinum found by difference, or the platinum may be precipitated as ammonium platinic chloride.

Alloys of gold, silver, and platinum are cupelled to remove base metals, and are then inquarted with a sufficient excess of silver (p. 525). If the gold present is less than ten times the weight of platinum, gold is also added to give this ratio. The prill is then parted in boiling sulphuric acid, leaving a residue of gold and platinum. This is again inquarted with silver, and is then parted in nitric acid, which dissolves silver and platinum. The gold is weighed, and the platinum found by difference, or the platinum is recovered with sulphuretted hydrogen as described above (Rose, "Precious Metals," 272; Trans. Amer. Inst. Min. Eng. 1912, **43**, 439; Met. and Chem. Eng. 1912, **10**, 219).

Silver ores may be assayed in the same way as gold ores of a similar kind (p. 524), but the scorification method is more usual, as large ore charges are seldom necessary. From 0·1 to 0·5 A.T. of the ore is mixed with 40 g. of granulated lead in a dry scorifier, and covered with a similar quantity of granulated lead. About 1 g. of borax is spread on top of the charge, and the scorifier is placed in a muffle heated to about 1,100°C. As soon as the charge is molten, the door of the muffle is opened slightly to give a good supply of air. The lead oxidises to litharge, which forms a ring of slag round the bath, oxidising sulphur, etc., and slagging the gangue minerals. This ring of slag slowly encroaches on the "eye" of metal and finally covers it. A pinch of anthracite powder, wrapped in tissue paper, is then dropped on the surface to reduce a little lead and so clean the slag, and, when the fusion is again tranquil, the charge is poured into a mould. The slag, which will still carry a little silver, is crushed, and then cleaned by crucible fusion. The two lead buttons are cupelled at a reasonably low temperature to prevent excessive loss of silver by volatilisation. The loss during cupellation is estimated by cupelling a similar, known weight of silver with the corresponding quantity of lead (Bugbee, "Fire Assaying," Chapman and Hall, 1933, 127).

Silver bullion and alloys may be assayed by direct cupellation if over 700 fine. The amount of lead required varies from six to twelve times the weight of silver present, depending on the fineness. Cupellation, which removes the base metals, is conducted at a low temperature, but must be finished above the melting-point of silver (961°C.), in order to remove the last of the lead. The muffle is then closed, to exclude draughts, and is cooled slowly to prevent loss of silver by spitting. The prills are hammered, brushed clean, and weighed. Losses during cupellation vary from 5 to 15 parts per 1,000, and check assays, made to a similar composition, are placed in various parts of the muffle to measure and correct for these losses. Any gold present is weighed as silver.

In the Indian Mint method the alloy is dissolved in nitric acid and the silver is precipitated with a slight excess of hydrochloric acid. The silver chloride is coagulated by shaking, and is washed, dried, and weighed. Any gold is weighed as silver chloride. This is the best method for alloys which are less than 700 fine (Hughes, Trans. Inst. Min. and Met. 1908, **17**, 334).

When the approximate composition of the alloy is known, volumetric methods are preferred. A weight of bullion or alloy containing about 1·003 g. of silver is dissolved in nitric acid, and nitrous fumes are removed. In the Gay-Lussac process 100 ml. of a standard solution of common salt (called a "normal" solution) are added from an automatic pipette, the strength being such that 1 g. of silver is precipitated. The mixture is shaken in a stoppered bottle to coagulate the precipitate, settled, and tested with a "decimal" solution of salt (one-tenth the strength of the normal solution). The appearance of the cloud of silver chloride formed gives a measure of the amount of silver left in solution. Further shakings and additions of the decimal solution are made if required. If the first addition of the decimal solution gives no precipitate, more silver is added in the form of a decimal silver nitrate solution. Pure assay silver is used to standardise the normal solution, from which the decimal solution is prepared by accurate dilution. Mercury and tin are precipitated with the silver. The interference of the former is prevented by the addition of sodium acetate and a little acetic acid, and that of the latter by the introduction of some tartaric acid (Percy, "Gold and Silver," John Murray, 1880, 282). In the Volhard method a similar procedure is followed, but the standard solutions are prepared from ammonium thiocyanate, and iron alum is used as an indicator. Titration with the decimal solution is continued to the appearance of a red-brown coloration. Check assays on fine silver are used as in the previous case (E. A. Smith, Trans. Inst. Min. and Met. 1907, **16**, 154).

Tin in ores may be estimated by the vanning assay described on p. 519. Ores of a similar nature should give comparable results, although losses vary with different manipulators. Considerable accuracy is obtained by skilled operators, the chief source of error, in certain localities, being the concentration of other heavy minerals, such as columbite and wolframite, with the cassiterite. The tin content is usually reported in pounds of "black tin" (impure tin oxide, assumed to contain 70% of tin metal) per ton of 2,240 pounds. This assay gives results which are comparable with those obtained in large-scale dressing plants, and is of value for that reason (Beringer, "Assaying," 273).

Tin concentrates, obtained either from dressing plants or from the vanning assay, may be treated by fusion with potassium cyanide. The sample is fused with about twice its weight of the flux in a wind furnace for 15 to 30 minutes. The charge is then poured into a mould or, better, is allowed to cool in the crucible, which is broken to recover the tin button. A little tin being lost in the slag, very high-grade concentrates give low results, whereas, owing to the reduction of other base metals, low-grade materials usually give high results. Approximately correct figures should be obtained with a 70% concentrate. Carbon may be mixed with the cyanide to give almost complete reduction of tin and base metals, the resulting button being assayed for tin by the wet method.

The Pearce-Low assay is in very general use for tin ores. A suitable weight of the crushed sample is brought to quiet fusion with sodium peroxide in an iron or nickel crucible. When cold, the mass is extracted with water and acidified with hydrochloric acid. The tin solution is reduced by suspending in it a coil of sheet nickel and boiling for ½ to 1 hour, the time required depending on the volume. The solution is cooled under an atmosphere of carbon dioxide, and is titrated with iodine. In well-equipped laboratories the hydrogen reduction assay is convenient. The sample is mixed with lime and heated to dull redness in a porcelain crucible, a stream of hydrogen being passed in through a Rose crucible lid. The reduced metals are dissolved in hydrochloric acid, and interfering metals are precipitated with *ferrum redactum*. After filtration, the tin is reduced by boiling with aluminium ribbon, and the tin sponge is redissolved in hydrochloric acid. The solution is cooled under carbon dioxide and titrated with iodine solution, the latter containing a large excess of potassium iodide to inhibit the interference of titanium (Mining Mag. 1929, **40**, 25).

Tin in alloys is determined by titration with iodine after reduction with iron or nickel sheet, or with finely powdered metallic antimony. Boiling solutions of stannous chloride, strongly acidified with hydrochloric acid, may be titrated with ferric chloride, which acts as its own indicator. Any metals which are precipitated during reduction, such as antimony or copper, must be removed before titration.

Titanium in ores and concentrates is brought into solution by fusion with potassium bisulphate and extraction with hydrochloric acid. Reduction is effected with metallic zinc, either in a Jones reductor or by boiling with a sufficient quantity of the 20-mesh metal. The warm reduced solution is titrated with ferric alum, using either ammonium thiocyanate or methylene blue as indicator. The latter reagent is rendered more sensitive by adding one drop of a 10% solution of sodium salicylate (Knecht and Hibbert, "Volumetric Analysis," Longmans, Green, 1925, 64, 72). Smaller quantities of titanium may be precipitated as TiO_2 with sulphur dioxide in a boiling, slightly acid solution, after any phosphorus and aluminium have been removed by fusion with sodium carbonate and extraction with water. The colorimetric method is based on the yellow colour produced by hydrogen peroxide with a 5% sulphuric acid solution of the titanium. Fluorides must be absent, and equal quantities of iron and phosphoric acid should be present in both assay and standard solutions to avoid interference (Scott, "Chemical Methods for Analysis of Metallurgical Products," 593, 597).

Titanium in steel is determined by the colorimetric method. When vanadium is present, a preliminary separation is made by boiling with thiosulphate in dilute hydrochloric acid solution, which precipitates TiO_2. In ferro-titanium a volumetric method is preferred (Lundell, Hoffman, and Bright, "Analysis of Iron and Steel," 356, 510).

Tungsten ores are decomposed by digestion with hydrochloric acid, and tungstic oxide is separated by repeated evaporation with aqua regia and nitric acid. This separation is not quite complete, and the last traces may be precipitated as cinchonine tungstate. After filtration and washing, the residue is dissolved in ammonia or ammonium carbonate and is evaporated to dryness in platinum, ignited, and weighed. Any silica is evolved with hydrofluoric acid (Scott, "Chemical Methods for Analysis of Metallurgical Products," 610).

Tungsten in steel is determined in a similar manner, by solution in hydrochloric acid and oxidation with nitric acid. After removal of silica, the impure tungstic acid is weighed, fused with sodium carbonate, leached with water, and filtered. The insoluble material is dried, ignited, and weighed, and the tungsten is determined from the loss in weight (United Steel Co.'s Standard Methods of Analysis, 1933, 13).

Uranium ores are decomposed with acids, and the heavy metals are removed as sulphides. Rare earth metals are precipitated as oxalates in weakly acid solution, and other interfering metals as carbonates. After removal of carbon dioxide, the uranium is precipitated with ammonia and ignited to U_3O_8, or is precipitated as phosphate in acetic acid solution. In the latter case it is ignited to uranyl pyrophosphate (Low, "Technical Methods of Ore Analysis," 239). Volumetric methods include the reduction of the uranium with zinc followed by titration with potassium permanganate, and the precipitation of the phosphate by titration with a standard phosphate solution, using ferrocyanide as an external indicator.

Vanadium.—A suitable quantity of ore is mixed and sintered with sodium peroxide in an iron crucible. The residue is leached with water and acidified with sulphuric acid. The solution is tinted with potassium permanganate, the excess of which is carefully removed with a minimum of ferrous sulphate. The vanadium is then reduced by titration with ferrous sulphate, adding about 2 ml. in excess after a faint blue colour is shown on the spot plate with ferricyanide. This excess is titrated with potassium dichromate, the vanadium being calculated from the difference in the two titration readings (Scott, "Chemical Methods for Analysis of Metallurgical Products," 631).

Vanadium in steel is determined in a similar manner. The sample is dissolved in sulphuric acid and the solution is oxidised, first with nitric acid, and then by boiling with permanganate. After cooling, the vanadium and chromium are both reduced with ferrous sulphate, and the excess of the latter and the vanadium are oxidised, in the cold, with permanganate. The vanadium is then reduced with an excess of ferrous sulphate, the excess being determined by titration with potassium dichromate (Johnson, "Chemical Analysis of Special Steels," Chapman and Hall, 1920, 4). Vanadium is also determined by a colorimetric method based on the colour produced by hydrogen peroxide (Sisco, "Analysis of Steel," McGraw-Hill, 1923, 255).

Zinc in ores is determined by titration with potassium ferrocyanide in faintly acid solution, after removal of all interfering metals. The normal group separation is usually followed, the manganese being removed with bromine and ammonia. Bromine is expelled by boiling, the last trace being destroyed by a small addition of hydrogen sulphide water. In Low's method the hydrochloric acid solution of the ore is repeatedly evaporated with nitric acid to remove chlorides, and is oxidised by evaporation, just to dryness, with potassium chlorate. Zinc is leached from the residue with a solution of ammonia and ammonium chloride, and the filtered extract is acidified with hydrochloric acid and saturated with sulphuretted hydrogen to precipitate copper. The sulphide precipitate need not be removed unless it is very bulky. Titration is carried out just below the boiling-point, uranium nitrate or acetate being used as an external indicator. If the standard solution contains a little ferricyanide, a small crystal of ferrous sulphate may be added to form an internal indicator (Low, "Technical Methods of Ore Analysis," 252).

Zinc in alloys is determined gravimetrically by precipitation as phosphate in a faintly acid acetic solution, after separation of all interfering metals. The determination of metallic *zinc in zinc dust* is made by measuring the volume of hydrogen evolved by the action of dilute sulphuric acid.

In the analysis of *commercial zinc* the metal is attacked with dilute sulphuric acid and filtered before the whole of the zinc is dissolved. Lead, cadmium, and any copper and tin are in the undissolved residue, and are taken up with nitric acid and separated as usual. Iron is determined on a separate sample by solution in acid and direct titration. Arsenic is evolved as arsine by dissolving the metal in hydrochloric acid. This gas is absorbed and oxidised in nitric acid, and the arsenic is precipitated with magnesia mixture.

Silica.—When the silica is mainly present as quartz, an acid attack followed by baking leaves a residue which is commonly reported as "silica and insolubles." This residue may be treated with hydrofluoric acid to determine the actual silica content. For greater accuracy the acid-insoluble portion is fused with fusion mixture, extracted, acidified, evaporated and baked. The residue is taken up with hydrochloric acid, filtered, and the filtrate is again evaporated and baked. When silica is high, this treatment must be repeated so long as any insoluble material is recovered. The combined residues are treated with hydrofluoric acid to determine the actual silica content. In certain cases rapid determinations can be made by fusion with potassium bisulphate, acid leaching and filtration. Results will be slightly low, but may be sufficiently accurate for many purposes.

Sulphur is determined by precipitation as barium sulphate after separation of silica. Soluble ores are attacked with oxidising mixtures such as aqua regia and bromine, nitric acid and potassium chlorate, etc., and insoluble ores by fusion of the insoluble portion with fusion mixture and nitre, followed by water extraction and filtration. Rapid results are obtained by fusion with sodium peroxide in a nickel crucible, solution in hydrochloric acid, destruction of the peroxide, and direct precipitation in the boiling solution.

Phosphorus.—After separation of silica the phosphorus is collected in the iron group precipitate, more iron being added for this purpose when necessary. The precipitate is redissolved in nitric acid, and the phosphorus is precipitated as ammonium phosphomolybdate. The latter is usually redissolved in ammonia, and the phosphorus is reprecipitated with magnesia mixture.

Coal.—The standard methods for the analysis of coal are described elsewhere (*v.* FUEL). The following rapid methods are used when only approximate results are required.

Moisture is determined by drying in a water or steam oven at 105°C. to constant weight. *Coking power* is examined by heating 50 g. of 30-mesh coal in a fireclay crucible, the lid of which is luted in place with fireclay. The evolution of gas is completed in about 20 minutes at a full red heat. After cooling, the coke is weighed and examined, the loss of weight giving a measure of the *volatile matter*. The *ash* is determined by igniting a thin layer of coal in a porcelain or, better, platinum dish in a muffle furnace, until combustion is complete. The sample should be stirred from time to time to prevent coking. The *calorific value* is determined in the Thompson calorimeter. 2 g. of coal are mixed with a suitable excess of a mixture of three parts of potassium chlorate and one part of nitre. By using 2,000 ml. or 1,934 ml. of water in the calorimeter, the calorific value or the evaporative power is determined direct from the rise in temperature, 10% of the latter being added to correct for the water equivalent of the apparatus and the losses inherent in the method. For *sulphur* the sample is ignited at dull redness with a mixture of two parts of magnesia and one part of potassium carbonate. When decomposition is complete, the residue is oxidised with bromine water, acidified with hydrochloric acid, and filtered. After removal of silica, sulphur is precipitated as usual. *Phosphorus* is determined on the ash, of which a complete analysis may sometimes be required.

Cyanide Solutions.—In the control of a cyanide mill, constant analyses of the cyanide solutions are necessary in order to maintain them at the requisite strength, and to check extraction.

Gold and silver are determined by boiling a suitable quantity of the solution with lead acetate, hydrochloric acid and metallic aluminium or zinc. The precious metals are collected in the lead sponge, which is squeezed dry and cupelled. These metals are reported in troy oz. or dwts. per ton (avoirdupois) of solution. Free cyanide is found by direct titration with a standard solution of silver nitrate, a few drops of potassium iodide solution being used as an internal indicator. If soluble sulphides are present, they are removed by agitation with freshly precipitated lead carbonate. On conclusion of this titration, *protective alkali* is determined by adding phenolphthalein and titrating with standard acid. *Total cyanide* is found by titrating a fresh sample with silver nitrate after destroying the combined cyanides with caustic soda. *Total alkali* (including cyanide) is determined by direct titration with standard acid, using methyl orange as indicator. Cyanides are, for convenience, reported as the percentage of potassium cyanide in the solution, and alkalis either as the percentage of caustic potash, or as lb. of lime (CaO) per ton of ore treated. *Reducing power* is measured by the volume of $N/10$ potassium permanganate required for the titration of 100 ml. of solution which has been acidified with sulphuric acid (Clennell, "Chemistry of Cyanide Solutions," McGraw-Hill, 1910).

C. W. D.

ASTACIN, $C_{40}H_{48}O_4$, a carotenoid pigment widely distributed in marine invertebrates, crystallises from aqueous pyridine in metallic deep violet needles, m.p. 240°–243°. The pigment shows one broad absorption band with its apex at 500 mμ in pyridine and at 510 in carbon disulphide; it is optically inactive and reacts towards alkalis as an acid.

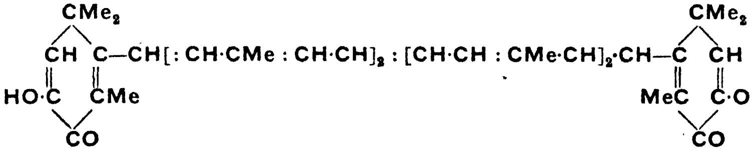
Astacin was first definitely characterised by Kuhn and Lederer (Ber. 1933, **66** [B], 488), who employed the lobster (*Astacus gammarus*) as their source. The pigment exists as a red, fat-soluble lipochrome and as greenish-brown water-soluble chromoprotein complexes. Acetone, dilute mineral acids or boiling water effect a cleavage of the protein portion, the entire animal then appearing red. The distribution of pigment in the lobster is shown in the appended table (Kuhn and Lederer, *l.c.*). The ovo-ester crystallises from aqueous pyridine in rhomboids, m.p. 245°–248°.

NORWEGIAN LOBSTER (weight 500 g.)

Shell.	Hypodermis.	Eggs.
Dark brown chromoprotein	Red lipochrome	Greenish chromoprotein
↓ HCl and acetone	↓ acetone	↓ acetone
Red astacin ester	Red astacin ester	Red astacin ovo-ester
↓ NaOH	↓ NaOH	↓ NaOH
Astacin (3–4 mg.)	Astacin (7–8 mg.)	Astacin (2–3 mg.)

Astacin has also been isolated from the sea-spider (*Maja squinado*), the prawn (*Nephrops norvegicus*), the angler fish (*Lophius piscatorius*), starfish, *i.e.* *Ophidiaster ophidianus*, and its occurrence in other similar forms of life is probably frequent (*cf.* Sörensen, Z. physiol. Chem. 1935, **235**, 8; Lederer, Compt. rend. Soc. Biol. 1934, **117**, 1086). Sörensen (*l.c.*) has recently shown that the "salmenic acid" of v. Euler, Hellström, and Malmberg (Svensk Kem. Tidskr. 1933, **45**, 151), the pigment of salmon flesh, is actually astacin.

The constitution of astacin has been elaborated by Karrer and his colleagues. Karrer and Loewe (Helv. Chim. Acta, 1934, **17**, 745) showed that astacin possessed thirteen double bonds and that of the four oxygen atoms two exhibit ketonic properties (preparation of a dioxime) and two are enolic; they showed further that these groups must exist in adjacent pairs, as a di-phenazine derivative is formed with *o*-phenylenediamine. The structural formula was deduced from controlled oxidation; Karrer, Loewe, and Hübner (Helv. Chim. Acta, 1935, **18**, 96) treated the di-phenazine derivative with potassium permanganate and obtained αα-dimethylsuccinic acid, whereas oxidation of astacin itself gives rise to dimethylmalonic acid. Such results (*see* CAROTENOIDS) indicate the following formula for astacin:



I. M. H. and R. F. P.

ASTERIA (*Star Sapphire*) *v.* CORUNDUM.

ASTERIC ACID, $C_{28}H_{40}O_4$, the carotenoid pigment of various starfish, *e.g.* *Crossater paposus* and *Solaster endica*, exists in the animal as a blue, water-soluble chromoprotein complex. The pigment was first isolated by v. Euler and Hellström (Z. physiol. Chem. 1934, **223**, 89), who showed that alcohol effected an instantaneous cleavage, yielding the red, fat-soluble lipochrome and the protein; exposure to air caused reunion of these fragments. Asteric acid separates from light petroleum as a deep violet crystalline powder, m.p. 185°, and shows absorption maxima in ether at 490 and at 457 mμ. The acidic nature of the pigment is established by the formation of a copper salt.

I. M. H. and R. F. P.

ASTERIN. One of the two anthocyanin pigments occurring in the flowers of the purple-red aster, *Callistephus chinensis* Nees (*Aster chinensis* L.), from which it was isolated and identified as a monoglucoside of cyanidin by

Willstätter and Burdick (Annalen, 1917, **412**, 1149). They separated it from *callistephin*, the monoglucoside of pelargonidin, by fractional precipitation from alcohol by ether, isolating the hydrochloride $C_{21}H_{21}O_{11}Cl\cdot 1\frac{1}{2}H_2O$ in red-brown prisms. Asterin was shown by Willstätter and Robinson (Ber. 1928, **61** [B], 2503) to be identical with the other natural cyanidin 3-monoglucoside *chrysanthemin* (*q.v.*).

R. S.-M.

ASTRALINE. Russian petroleum oil, used for burning.

ASTRALIT. This somewhat sensitive explosive has been used as a filling for trench mortar bombs, rifle grenades, etc., where the shock of discharge is not so severe as in the case of projectiles fired from guns. It varies somewhat in composition, a typical formula being ammonium nitrate 84·5%, trinitrotoluene 7%, paraffin oil 2·5%, wood meal 1%, charcoal 1%, nitroglycerin 4%. H. S.

ASTRALITE. A glass resembling aventurine, but containing crystals of a cuprous compound which by reflected light exhibit a dichroic iridescence of dark red and greenish-blue. Made by fusing and allowing to cool slowly a mixture of 80 parts silica, 120 lead oxide, 72 sodium carbonate, 18 borax, with either 24 parts scale oxide of copper and 1 part scale oxide of iron, or with 5 parts lime, 26 copper oxide and 2 iron oxide.

ASTROLIN. Trade name for antipyrine-methyl-ethyl glycollate, $C_5H_{10}O_3,C_{11}H_{12}ON_2$, m.p. 64°–65·5°. A colourless powder, with a slight smell and pleasant taste, readily soluble in water and alcohol.

ASTROPHYLLITE *v.* APATITE.

ASYPHIL. Trade name for a *mercury salt of p-aminophenylarsonic acid*,

$$(H_2N\cdot C_6H_4\cdot AsO(OH)O)_2Hg.$$

A.T.=long assay ton=32·67 g. (*v.* ASSAYING).

ATACAMITE. Hydrated oxychloride of copper, $CuCl_2\cdot 3Cu(OH)_2$, occurring in the Atacama region of Chile, sometimes in sufficient amounts for use as a copper ore (Cu 59·4%). Large quantities have also been mined at Wallaroo in South Australia. Orthorhombic crystals of a bright green colour and with brilliant faces are not uncommon. Sp.gr. 3·76. Before the days of blotting-paper, it was used, under the name of arsenillo, as a writing sand for absorbing ink. L. J. S.

ATEBRINE *v.* ACRIDINE DRUGS.

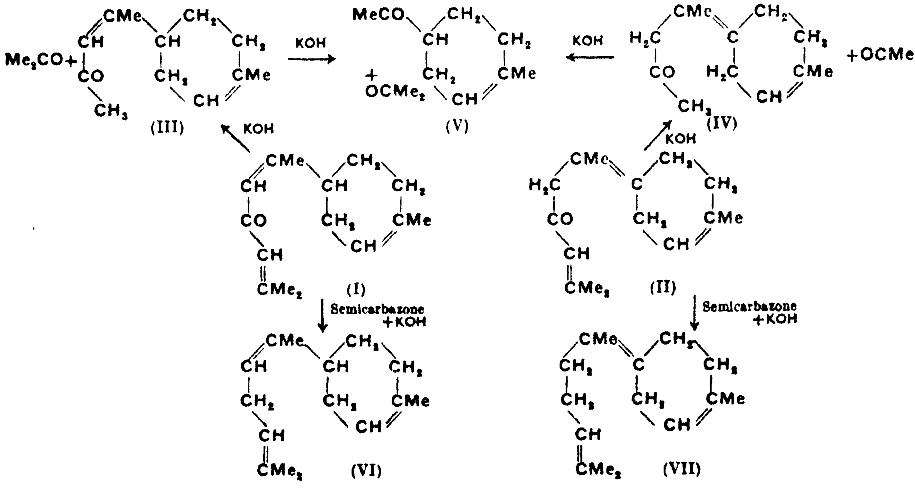
ATELESTITE. A bismuth arsenate found as minute, yellow, monoclinic crystals at Schneeberg in Saxony: Bi_2O_3 82·41, As_2O_3 14·12, H_2O 1·92%.

ATIS ROOT. *Aconitum heterophyllum*, contains non-poisonous alkaloids and much starch. Tonic.

ATISINE *v.* ACONITINE AND THE ACONITE ALKALOIDS.

ATLANTONE. The true cedar-wood oils from *Cedrus atlantica* Manet and *C. deodara* Loud. have been shown by St. Pfau and Plattner (Helv. Chim. Acta, 1932, **15**, 1481; 1934, **17**, 129) to contain, amongst other high-boiling constituents, two sesquiterpene ketones, *α-atlantone* and *γ-atlantone*. Whilst it has not proved possible to separate the two ketones in a state of purity, since they do not yield any crystalline derivatives, St. Pfau and Plattner have established their structures by an ingenious series of experiments.

α-Atlantone is represented by (I). It yields on digestion with alkali *acetyl dipentene* (III) and acetone, the former breaking down on further treatment with the same reagent into 1-*methyl*-4-*acetyl*-Δ^1-cyclo*hexene* (4-*methyl*-Δ^3-*tetrahydroacetophenone*) (V), and a second molecule of acetone. Distillation of α-atlantone semicarbazone with potassium hydroxide gives *α-bisabolene* (VI).



By a similar series of reactions *γ-atlantone* II yields *acetyl terpinolene* (IV) and acetone and finally 1-*methyl*-4-*acetyl*-Δ^1-cyclo*hexene* (V), whilst from the semicarbazone *γ-bisabolene* (VII) was obtained.

The structures assigned to these two ketones were confirmed by a study of the oxidation and reduction products. The facility with which these ketones are hydrolysed by alkali accounts for the fact that Roberts (J.C.S. 1916, **109**, 791) and Simonsen and Rau (Indian Forest Rec. 1922, **9**, 13) erroneously considered 1-methyl-4-acetyl-Δ^3-*cyclo*hexene to be a constituent of the essential oil.

The true cedar-wood oils are used, more especially in France, as a substitute for sandalwood oil (Massy, Parfumerie Moderne, 1929, 177). J. L. S.

ATMOSPHERE. The gaseous envelope surrounding any liquid or solid body, more particularly denoting the gaseous envelope surrounding the earth, which is commonly known as air. The earth's atmosphere has no definite outer boundary, but the pressure and density diminish slowly with height. The presence of oxygen and nitrogen at heights of several hundreds of kilometres above the ground is known from the lines in the spectra of aurora, and from the study of ionisation in the upper atmosphere by means of wireless waves.

The pressure may be measured in terms of the height of the column of mercury which the atmosphere is capable of sustaining at any point. Physically it is preferable to regard the pressure as measuring the weight or mass of air above unit horizontal area. The pressure at any spot is subject to considerable variations from time to time, on account of the transfer of large volumes of air of differing densities horizontally from one region to another. Pressure is measured in inches of mercury, in millimetres of mercury, or in millibars. The millibar is defined as a force of 1,000 dynes per cm.^{2} The mean pressure over the earth's surface at mean sea-level is about 30 in. or 760 mm. of mercury, or about 1,013 millibars (mb.). The units are more accurately defined as under :

Mercury inch = 1 in. of mercury at 32°F. in latitude 45° = 33·8632 mb.

Mercury millimetre = 1 mm. of mercury at 0°C. in latitude 45° = 1·33322 mb.

760 mm. of mercury at 0°C. in latitude 45° = 1013·25 mb.

For all practical purposes, the mercury millimetre may be taken as 1⅓ millibars.

The unit of pressure known as an *atmosphere* is roughly the mean pressure over the earth. In British measures it is equivalent to 29·905 in. of mercury at 32°F. at London, which is equivalent to about 14·73 lb. per sq. in. In the metric system the *atmosphere* is the equivalent of a pressure of 760 mm. of mercury at 0°C. at Paris, and is equal to 1·033 kilograms per cm.^{2} The British *atmosphere* is thus 0·99968 of the metric *atmosphere*.

The density of dry air at 0°C. and 760 mm. is 1·2928 g. per litre. The pressure p, specific volume v, density ρ, and absolute temperature T, of dry atmospheric air are related by Boyle's Law, $pv = RT$, or $p = R\rho T$, where

$R = 2{\cdot}8703.10^3$ when p is in millibars and v in c.c. per g.

$R = 2{\cdot}8703.10^6$ when p is in dynes/cm.^{2} and v in c.c. per g.

$R = 2{\cdot}1529.10^3$ when p is in millimetres and v in c.c. per g.

The percentage composition by volume of dry atmospheric air is :

Nitrogen	78·08
Oxygen	20·94
Argon	0·9325
Carbon dioxide	0·03
Neon	0·0018
Helium	0·0005
Krypton	0·0001
Xenon	0·000009
Radium Emanation	6×10^{-18}

While these figures are generally accepted, it must be emphasised that the constitution of the atmosphere has not been thoroughly investigated with the most modern technique. The values given above for nitrogen, oxygen and carbon dioxide are those given in "International Critical Tables." Near the soil the percentage of these gases may show considerable variation from the values tabulated above (*see* Waksman, "Principles of Soil Microbiology," 2nd ed., Baltimore, 1932, 562). Tables of the composition of air usually show hydrogen as forming 0·01 %, but this value is certainly overestimated. Recent accurate work shows that the proportion of hydrogen is much less than 0·01 %, possibly even zero. Günther and Paneth (Z. physikal. Chem. 1935, A, **173**, 401) found the hydrogen content of air to be less than 0·0002 %. Determinations of the rare gases are conflicting, the values given in the table above being those accepted by Rabinowitsch after a very thorough and critical discussion ("Die Edelgase," Abegg's "Handbuch der Anorganischen Chemie," IV, iii, pt. 1, p. 19, Leipzig, 1928). These tabulated values are in close agreement with those of Moureu and Lepape (Compt. rend. 1926, **183**, 171).

In the lowest 17 km. of the atmosphere no variation in the composition of dry air has been clearly established. A recent determination by Paneth (Nature, 1935, **136**, 717) appears to indicate that the proportion of helium is 20% greater at 25 km. than at the surface. The sharp termination of the solar spectrum at 0·2890μ, even when photographed at 9 km. above the earth, was shown by Hartley to be due to ozone. Recent work by Dobson and various collaborators (*see* esp. Dobson, Götz and Meetham, Proc. Roy. Soc. 1934, A, **145**, 416) has shown that the proportion of ozone to other gases increases from the ground upwards, to levels of about 35 km., and then decreases. Chalonge and Götz (Compt. rend. 1929, **189**, 704) have shown that the relative proportion of ozone increases rapidly with height above the ground. The total amount of ozone, if collected together at 0°C. and 760 mm., would on the average form a layer of thickness 0·3 cm., with variations of

25% above and below the mean (Fabry and Buisson, Mémorial des Sciences Physiques, Acad. Sci., Paris, Fasc. xi, 1930). The total increases from equator to pole, and shows a maximum in spring and a minimum in autumn; it also shows a variation with surface pressure, the total of ozone in the rear of a depression being greater than the normal amount in any part of the atmosphere. Ozone is only present in the surface layers of the atmosphere in very minute quantities (Fabry and Buisson, Compt. rend. 1931, **192**, 457; Götz and Ladenberg, Naturwiss. 1931, **19**, 373). Wulf (Physical Rev. 1932, **41**, 375) ascribes its presence in part to photo-chemical action on the polymer of oxygen, O_4.

The composition of the atmosphere at great heights, say 100 km. or more above the ground, is not known with certainty. The base of the aurora is at an average height of about 100 km. The "green auroral line" in the spectrum of the aurora was shown by McLennan and Shrum (Proc. Roy. Soc. 1925, A, **108**, 501) to be due to atomic oxygen, the line being produced in transitions of atomic oxygen from one metastable state to another; while other bands in the spectrum are known to be due to nitrogen. These facts show that oxygen and nitrogen are both present at a height of 100 km., and perhaps for several hundred km. above this. The results are borne out by the existence of the ionised layers, known as the Kennelly-Heaviside and Appleton layers respectively, which are found at levels of 100 km. and 220 km. above the ground. The lower of these layers is ascribed to the ionisation, mainly of nitrogen, by uncharged particles from the sun; and the higher layer is produced by the ionisation, mainly of atomic oxygen, with possibly a small proportion of molecular oxygen and nitrogen, by ultra-violet rays from the sun.

Air also contains a minute but variable quantity of ammonia, mainly as carbonate. By aspirating from 10 to 20 litres of air through Nessler's solution (an alkaline solution of potassium mercury iodide), and comparing the depth of colour with that produced by a standard solution of an ammonium salt, H. T. Brown (Proc. Roy. Soc. 1870, **18**, 286) found, in Burton-on-Trent in autumn 1869, that samples of air taken at 2 m. above the ground contained from 0·4 to 0·9 part of $(NH_4)_2CO_3$ in 100,000 parts of air, whereas country air contained only 0·5 to 0·6 part in the same volume.

Nitrous and nitric acids are present in even more minute quantities than ammonia, accounting for only 1 part in from 1 to 3 million parts of air. The production of nitrous acid among the ions produced by flames has been shown by J. H. Coste and H. L. Wright (Phil. Mag. 1935 [vii], **20**, 209). The presence of nitrous acid in air can be detected by means of the Griess-Ilosva reagent, which yields a pink colour with nitrous acid, the colour being due to the diazotisation of one amine and coupling with the other in the reagent.

The variability of the proportions of the gases nitrogen, oxygen, and carbon dioxide in air near the soil has been referred to above. For the methods of determining the oxygen content of air, *see* CHEMICAL ANALYSIS, *Gas Analysis*.

The presence of carbon dioxide in the air was first demonstrated by Black in 1752. In normal air it forms about 0·03% by volume; in large towns the proportion is larger, particularly in foggy weather, when turbulent diffusion is reduced to a minimum. In the air of the country the proportion is slightly greater by night than by day, and the proportion in air near the soil varies considerably. Over the sea the proportion is reputed to be only about two-thirds of that over the land.

Non-gaseous Constituents of the Atmosphere.—The atmosphere contains in suspension, in addition to the condensation nuclei and the large and small ions referred to below, a certain amount of dust, organic matter such as pollen, and products of combustion from chimneys. Except for the local pollution by chimneys, the total amount of the solid matter suspended in the air is very small in amount. Methods of investigation of the pollution of the atmosphere are described in detail in "The Smoke Problem of Great Cities," London, 1925, by Shaw and Owens. The Annual Report of the Committee on Atmospheric Pollution, published by the Department of Scientific and Industrial Research, gives summaries of observations of pollution made in a number of towns in Great Britain. It is found that the small solid particles in the atmosphere, when observed at not less than one mile away from chimneys or other immediate sources of pollution, have a mean diameter of about $\cdot 85\mu$, the limits of size being usually $0{\cdot}3\mu$ to $1{\cdot}7\mu$. The action of these solid particles in cutting off sunlight, and particularly ultra-violet light, is their most direct effect upon human life.

Water Vapour in the Atmosphere.—The quantity of water vapour in the atmosphere varies within wide limits, the amount in saturated air depending on the temperature. The extent to which the partial pressure of water vapour varies with temperature may be gathered from the following brief table:

Over ice.	Partial pressure in *mb.*	Over water.	Partial pressure in *mb.*
0°C.	6·1	−10°C.	2·9
−10°C.	2·6	0°C.	6·1
−20°C.	1·0	10°C.	12·3
−30°C	0·4	20°C.	23·4
—	—	30°C	42·5
—	—	40°C.	74·1
—	—	50°C.	123·4
—	—	60°C.	199·1
—	—	70°C.	311·6

The number of grammes of water vapour per gramme of dry air will be inversely proportional to the partial pressure of the dry air. If e be the partial pressure of the water vapour, and p the total pressure, the number of grammes of water vapour to one gramme of dry air is $0{\cdot}622e/(p-e)$. Thus at an average atmospheric pressure, round about 1,000 millibars, near the surface of the earth, the number of grammes of water vapour to one kilogramme of dry air will be given by $\frac{5}{8}$ of the numbers tabulated above as the vapour-pressure in millibars. Thus at 0°C. there will be $\frac{5}{8} \times 6{\cdot}1$, say 3·8 g. of water vapour to one kilogramme of dry air.

The standard meteorological method of determining the water-vapour content of the air is by the use of a psychrometer, and more particularly the wet- and dry-bulb hygrometer, using tables to find the relative humidity, which express the vapour pressure as a percentage of the saturation value. The amount of water vapour in the atmosphere can be determined chemically by aspirating a given volume of air through weighed tubes filled with a hygroscopic substance, such as phosphorus pentoxide, afterwards re-weighing the tubes. The relative humidity varies within wide limits from day to day, sometimes reaching saturation, but in the British Isles seldom falling below 40%. The water-vapour content of the atmosphere shows only a slight variation in the course of the day, and so the relative humidity varies in the inverse sense to the temperature, being lowest in the middle of the afternoon, and highest in the early morning.

The relative proportion of water vapour in the atmosphere decreases with height above the ground, as a result of the decrease of temperature with height. Some idea of the rapidity of this decrease can be obtained from the following figures, which give the ratio of the densities of saturated water vapour and dry air at different heights, in an atmosphere in which the surface temperature is 12°C., and the temperature decreases with height at the rate of 6°C. per kilometre up to 10 km., and then remains steady up to 20 km.

	Temperature.	Ratio water vapour/dry air.
Surface .	12°C.	0·0092
10 km. . .	−48°C.	0·000097
20 km. . .	−48°C.	0·00044

Condensation in the Atmosphere.—It was shown by C. T. R. Wilson (Phil. Trans. 1897, A, **189**, 265) that in air from which all solid and liquid suspensions have been carefully filtered, condensation on ions will not commence until at least four-fold saturation is reached. Such a degree of supersaturation has never been observed in the atmosphere. Condensation actually takes place, not on ions, but upon small particles, known as *nuclei of condensation*, small crystals mainly of sulphates and chlorides, or droplets of nitrous acid, which are all hygroscopic. Ordinary dust such as the dust in a carpet or fine dust from a coal cellar will not act as nuclei of condensation. At inland places the effective nuclei are mainly products of combustion from domestic or factory chimneys, while over the oceans and the land bordering them large amounts of potential nuclei are supplied to the atmosphere by the evaporation of fine spray. That many nuclei come from the sea is shown by the apparently universal presence of chlorine ions in rainwater and in unpolluted river water. The fact that condensation takes place on a nucleus avoids a theoretical difficulty in explaining the formation of water drops in the air. Kelvin showed (Proc. Roy. Soc. Edin., Feb. 1870) that over a small water drop of radius r the saturation vapour pressure exceeds that over a plane surface by an amount which increases rapidly as r becomes very small. This would demand enormous supersaturation in the earliest stages of the formation of a water drop.

The standard method of counting nuclei in the atmosphere is due to John Aitken ("Collected Scientific Papers," Cambridge, 1923, p. 65), who invented a simple nucleus counter. A mass of air is subjected to sudden expansion, which produces sufficient cooling to yield considerable supersaturation, resulting in condensation on the nuclei in the form of visible drops, which can then be counted.

Many types of nuclei in the air are sufficiently hygroscopic to start condensation in air well below saturation. In sea fogs the nuclei begin to accumulate water when the relative humidity is about 75%.

Droplets of water in the atmosphere vary within very wide limits. In a country fog the droplets are between 4×10^{-4} cm. and 3×10^{-3} cm. in radius, and may number up to, say, 1,500 per c.c. Drops in a cloud may be as great as 10^{-2} cm. in radius, while raindrops vary from about 0·02 cm. in light drizzle to about 0·2 cm. in very heavy rain.

Atmospheric Electricity.—A charged electroscope slowly loses its charge in air, the leakage being greater in dry than in damp air. The conductivity of the air is due to the charge on the ions present. The surface of the earth carries a negative charge in normal conditions of fine weather, while the air is positively charged, the potential increasing from zero at the ground to about 300,000 volts at about 15 km. The ions in the atmosphere are conveniently classified as "small" and "large" ions. The small ions consist of agglomerations of up to 10 molecules, of radius 3×10^{-8} to 10×10^{-8} cm., carrying a single positive or negative electronic charge, and numbering 300 to 1,000 per c.c. The union of a small ion with a condensation nucleus produces a large ion, and of these there are usually present in the atmosphere 1,000 to 8,000 per c.c. These figures are rough averages of observations over land. Over the sea the number of large ions is usually much lower than over land, being of the order of 500 per c.c.

The current of electricity which flows from the air to the earth's surface, which is generally known as the "air-earth current," brings down to the earth about 60 coulombs per km.^{2} per annum. The mobility of the small ions being much greater than that of the large ions, the air-earth current is mainly due to the small ions. The number of positive small ions is greater than the number of negative small ions in the ratio 22 : 1, the greater mobility of the negative ions making for readier capture by condensation nuclei, with consequent change into large ions.

The principal ionising agencies in the atmosphere are radiations from radioactive substances in the earth, radiation from radioactive matter in the air itself, and the penetrating radiation or cosmic rays. In the earth's crust radium, thorium and their products are widely distributed, and so the surface of the earth emits

α, β, and γ rays into the air. The α rays penetrate through only a very thin layer of air, and their ionising effect is inconsiderable. The β rays come from a greater depth in the earth, and penetrate to greater distances in the air, and their effect is more considerable. The symbol I is usually employed to denote " one pair of ions produced per c.c. per sec." The effect of the β rays from the earth's surface is then described as varying from 1 I at the surface to 0·1 I at a height of 10 m. The γ rays come from still greater depths, and consequently from a still greater quantity of radioactive material. They produce an effect which on the average varies from about 3 I at the surface to 1·5 I at a height of 150 m., and to 0·3 I at a height of 1 km. The γ ray activity of potassium is not inconsiderable. It is inferred from analyses of samples of the earth's crust (Suckstorff, Naturwiss. 1931, **19**, 87) that at about 10 m. above the ground the contributions of radium, thorium C″ and potassium to the γ ray ionisation of air are in the ratios 1 : 1 : 0·7. The total ionising power of the earth's crust is from 2 to 10 I. The earth-radiation effect is negligible over the sea.

The atmosphere contains a considerable quantity of the radioactive emanations radon and thoron and their successive products. A wire charged electrically to a negative potential of a few hundred volts and exposed to the air collects a readily detectable quantity of radium A and thorium A, by recoil from the disintegration of these emanations. The gases arise from the decay of radium and thorium within the earth, from which they diffuse into the air, and are distributed through the lower atmosphere by turbulence. The ionising effect of the air-radiation is about 5 I near the earth's surface, 60% being due to radon and its α ray products and the remainder to the thoron series. The variation with height above the ground is not known with any degree of certainty, though observations show that at 5 km. the effect is less than 0·1 I. This effect is also very small over the oceans.

The ionisation by cosmic rays or the penetrating radiation lies between 1·5 I and 2·5 I, increasing rapidly with height, so that at 10 km. it is about ten times as effective as at the ground. The total ionising power at sea-level due to the three effects discussed above is given below in terms of I, *i.e.* the number of ion-pairs produced per c.c. per second.

	Over land.	Over sea.
Radioactive matter in the earth	4·0 I	0·0 I
Radioactive matter in the air .	5·0 I	0·0 I
Penetrating radiation	2·0 I	2·0 I
Total ionising power. . .	11·0 I	2·0 I

For further details of the known facts relating to atmospheric electricity reference may be made to a short but clear summary by B. F. J. Schonland in " Atmospheric Electricity " (London, 1932, Methuen and Co.).

The Vertical Distribution of Temperature in the Atmosphere.—Except in a shallow layer near the ground the fall of temperature with height, known as the *lapse-rate*, is approximately uniform, and equal to about 6°C. per kilometre of height, up to a certain limiting level, which occurs at a height which varies with latitude, being about 18 km. at the equator, 10 km. in latitude 50°, and 7 km. or even lower at the poles. The layer in which the temperature decreases steadily with height is known as the *troposphere*, and the level at which the fall is suddenly checked is known as the *tropopause*. Above the tropopause is the *stratosphere*, in which the temperature may remain constant, decrease slowly, or increase slowly, within a range of, say, 10 km. of height. Near the ground the lapse-rate shows wide variations, on sunny afternoons often surpassing the limiting value for stability (the dry adiabatic lapse-rate of 10°C. per kilometre), and on clear nights the temperature at the surface of the ground falling rapidly on account of radiation losses leads to a situation in which the temperature increases upward.

At heights above 20 km. no direct observations can be made, and our knowledge depends on observations of the travel of sound waves and of wireless signals. Observations of the travel of sound suggest that at a height of 50 km. the temperature is about 60°C. At still greater heights the temperature increases still further, and Appleton estimates from his observations of ionisation at heights of 220 km. and thereabouts that the temperature at 300 km. on a summer day exceeds 900°C. (*see* Appleton, Nature, 1935, **136**, 52).

The Physical Constants of Dry Air.—The specific heat of dry air is 0·2396 at constant pressure (c_p), and 0·1707 at constant volume (c_v); the ratio of the specific heats is 1·403 (Partington and Shilling, " The Specific Heats of Gases," London, 1924). The coefficient of thermal expansion is 0·0003665 per °C., between –30°C. and 200°C. The thermal conductivity at 0° C. is $5{\cdot}74\times10^{-5}$ cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$, and at 40°C. $6{\cdot}42\times10^{-5}$ in the same units (Hercus and Sutherland, Proc. Roy. Soc. 1934, A, **145**, 599; Kannuluik and Martin, *ibid.* **144**, 476). The coefficient of viscosity at 0°C. is $1{\cdot}71\times10^{-4}$ and at 40°C. $1{\cdot}90\times10^{-4}$.

The refractive index for the D line of sodium is 1·000292 for dry air, and 1·000257 for water vapour. For damp air at a total pressure p, and partial pressure of water vapour e, the index of refraction of the mixture for the D line of sodium is given by

$$\mu-1=\frac{pT_0}{p_0T}\left\{0{\cdot}000292-0{\cdot}000035\frac{e}{p}\right\}$$

where p_0 and T_0 are standard pressure and temperature, 760 mm. and 273°K.

Absorption and Radiation in the Atmosphere —The ozone layer, the centre of gravity of which is at a height of 22–25 km. above the earth's surface, absorbs 4–6% of the total incoming beam of solar radiation, this absorption taking place almost entirely in the Hartley band of ozone, 0·23μ to 0·32μ. For equal mass, ozone absorbs radiation of this wave-length more strongly than metals absorb visible light (0·4 to 0·8μ). Still more strongly, for equal mass, does oxygen absorb in the far ultra-violet, between 0·13μ and 0·175μ, and oxygen also absorbs in the Schumann-Runge system of absorption bands beyond 0·175μ, and in another band between 0·24μ and 0·28μ. It is probable that O_2 is converted into O_3 by the absorption of radiation in the band

0·20–0·22μ, and that the dissociation of O_3 into O_2 is effected by the radiation in the Hartley band.

As a result of the ultra-violet absorption at high levels, the solar spectrum, even when photographed at 9 km. above the ground, terminates sharply at 0·289μ. At ordinary temperatures there is no appreciable absorption of radiation by the elementary gases of the atmosphere, nitrogen, oxygen, argon, etc. (Burmeister, Verh. D. Phys. Ges. 1915, **151**, 612). Apart from the losses due to absorption by oxygen and ozone at high levels, the only true absorption losses from the solar beam on its way down through the atmosphere are those due to CO_2 and water vapour, and to organic matter present in the atmosphere, the loss due to the latter being very slight. There is a loss by scattering, either by the molecules or by small particles of solid or liquid matter held in suspension. The blue colour of the sky is explained by the effect of scattering by the molecules and small particles of dust, the scattering being much more effective in the blue than in the red end of the spectrum, so that a beam of scattered light is richer in blue than in red light. At increasing heights above the ground the decreasing density of matter capable of producing scattering leads to a darker colour of the sky, and at very great heights the sky should appear dead black.

The air is thus not heated by the direct rays of the sun, but by radiation from the ground, in a range of wave-lengths from about 3μ to about 100μ. Most of the absorption in clear air is by water vapour, with some absorption by CO_2, the latter being the only constituent of dry air which shows any appreciable effect at atmospheric temperatures in absorbing long waves in the region covered by radiation. CO_2 shows an intense band of absorption centred at about 14·7μ (Rubens and Aschkinass, Ann. Physik u. Chem. 1898, **64**, 584). Absorption by water vapour was investigated in great detail by Hettner (Ann. Physik, 1918, **55**, 476), who found the following main regions of absorption :

(*a*) Bands centred at 1·37μ, 1·84μ, and 2·66μ.

(*b*) A very intense band centred at 6·26μ.

(*c*) A wide band beginning at 9μ, and extending to the limit of Hettner's measurements at 34μ, and probably beyond it. This band shows the typical form of the rotation spectrum, the interval of frequency between consecutive lines in the band indicating a nearly linear molecule. The existence of lines of absorption beyond the limit of 34μ investigated by Hettner was demonstrated by earlier investigators, though it is not possible to state with certainty what is the structure of the water-vapour spectrum in the higher reaches of wave-length.

Hettner's observations were made on steam at 100°C., but the results are in general agreement with those of Fowle on the absorption of water vapour in the atmosphere, except that Fowle (Smithsonian Inst. Misc. Coll. 1917, **68**, 41) found no appreciable absorption in the range 8½–11μ. If in a path containing x cm. of precipitable water per cm.^{2} of cross section the transmission is 10^{-ax}, some idea of the values of a given by Hettner can be obtained from the following table :

Wave-length in μ	6·2	10	15	20	24	25	30	34
a	454	1	6	50	70	35	164	227

Thus a small amount of water vapour is sufficient to absorb completely all radiation of wave-length 15μ or above.

A detailed discussion of some applications of Hettner's measurements to atmospheric phenomena is given by Simpson (Mem. Roy. Met. Soc. 1928, III, No. 21) and by Brunt (Quart. J. Roy. Met. Soc. 1932, **58**, 389). Air is transparent to radiation of wave-lengths 3·5–4·5μ, and to wave-lengths 8·5–11μ. Simpson assumed that 0·3 mm. of precipitable water would be sufficient to absorb completely all radiations of other wave-lengths, and so obtained quantitative agreement with observed facts. From the fact that a small amount of water vapour is sufficient to absorb all radiation of the wave-lengths of the water-vapour bands in the spectrum it follows that the radiation which comes from the atmosphere down to the ground must have originated at relatively small heights above the ground. Brunt used this fact to derive an expression for the downward radiation from the atmosphere in the form $\sigma T^4(a+b\sqrt{e})$, where σT^4 is the total black body radiation at temperature T, e is the vapour pressure, and a and b are constants.

In discussing meteorological problems of this kind, it is assumed that the earth's surface is a perfect radiator, or black body. Some observation by W. H. Dines appear to show that this is substantially correct, whether the surface is bare earth, woodland, grass, sea, ice or snow, since the surface temperatures are always such that the radiation is of wave-lengths above 4μ, which are absorbed almost completely by every type of surface. The cooling of the ground on clear nights is largely due to the radiation in the bands of wave-length to which water vapour is transparent. There is no downward radiation from the atmosphere in these wave-lengths. Clouds absorb and radiate practically as black bodies, so that at night when the sky is covered with cloud there is a downward flow of radiation in all wave-lengths appropriate to the temperature of the cloud, which is sufficient to compensate for the greater part of the heat lost from the ground by its own radiation. As a result of this, the conditions during overcast nights remain nearly steady, the change of temperature in the course of the night being roughly proportional to the height of the cloud. During the day, when the sky is overcast, the cloud sheet reflects outward practically all the incoming radiation from the sun, and the normal afternoon rise of temperature is diminished, and frequently, with a sky completely overcast with low thick clouds, the temperature remains practically constant.

Explanation of the Stratosphere.—The substantial constancy of the temperature at all heights within the stratosphere was explained by Gold (Proc. Roy. Soc. 1909, A, **83**, 43) as due to the balance between the energy radiated from each element of the air and the energy absorbed by it. The theory is not complete in detail, and fails to account for the observed cases when the temperature increases with height within the stratosphere. Gold's theory was restricted to the consideration of radiation and absorption by water vapour. The recent discovery that the ozone in the upper air extends from the ground to a height of 40 km. indicates that the absorption by ozone is the important factor in accounting for the increase of temperature with height in the stratosphere, when this is observed.

Constitution of the Upper Air.—Earlier writers on the subject assumed that in the stratosphere and beyond it there would be no turbulent mixing of air from different levels, and that the distribution of the constituents of the atmosphere at those levels would be determined in accordance with Dalton's law. On this basis the lighter constituents must predominate at high levels, and the precise composition which we should calculate for the upper air would then depend on what assumptions are made as to the normal components of air. Thus Humphreys found (" Physics of the Air," Philadelphia, 1920, Chap. V.) that above 100 km. the atmosphere should consist almost entirely of hydrogen. Wegener ("Thermodynamik der Atmosphäre," Leipzig, 1911) assumed the existence of a constituent still lighter than hydrogen—*geocoronium*—and showed that at 100 km. the atmosphere should consist of about 70% hydrogen and 30% geocoronium, and that with increasing height the latter should predominate. Chapman and Milne (Quart. J. Roy. Met. Soc. 1920, **46**, 357), to whose paper reference should be made for details of the method of computation of the constitution of the upper atmosphere, assumed that hydrogen is not a normal constituent of the atmosphere, but that its occurrence is accidental, and that at higher levels it must in any case combine with oxygen. They found that above 100 km. the atmosphere should be almost entirely composed of helium. Later views tend to discredit the application of Dalton's law to this problem. The combined evidence of meteor trails, aurora, and the ionised layers associated with the names of Kennelly-Heaviside and Appleton shows that even at heights of several hundred kilometres oxygen and nitrogen are important constituents of the atmosphere.

Some Further References.—Methods of air analysis suitable for use in mining and other cases where a rapid analysis of the purity of air is required are described by J. S. Haldane and J. I. Graham, in " Methods of Air Analysis," London, 1935.

The meteorological aspects of the physics of the atmosphere are to be found in any textbook of the subject of meteorology. For the facts of observation, reference should be made in particular to Hann-Süring, " Lehrbuch der Meteorologie," Leipzig, 1926, or to Shaw, " Manual of Meteorology," vol. II, Cambridge, 1936. The theoretical aspects of the subject are discussed in Brunt, " Physical and Dynamical Meteorology," Cambridge, 1934. D. B.

ATOCIN, *Atophan, Cinchopen*, 2-phenylquinoline-4-carboxylic acid.

ATOMIC DATA OF THE ELEMENTS.

INTERNATIONAL ATOMIC WEIGHTS AND STABLE ISOTOPES, 1936 (O=16).

	Symbol.	Atomic No.	Isotopes.	Atomic Wt.
Aluminium	Al	13	—	26·97
Antimony	Sb	51	121 ; 123	121·76
Argon	A	18	36 ; 38 ; 40	39·944
Arsenic	As	33	—	74·91
Barium	Ba	56	135 ; 136 ; 137 ; 138	137·36
Beryllium	Be	4	(8) ; 9	9·02
Bismuth	Bi	83	—	209·00
Boron	B	5	10 ; 11	10·82
Bromine	Br	35	79 ; 81	79·916
Cadmium	Cd	48	106 ; 108 ; 110 ; 111 ; 112 ; 113 ; 114 ; 116	112·41
Cæsium	Cs	55	—	132·91
Calcium	Ca	20	40 ; 42 ; 43 ; 44	40·08
Carbon	C	6	12 ; 13	12·00
Cerium	Ce	58	140 ; 142	140·13
Chlorine	Cl	17	35 ; 37	35·457
Chromium	Cr	24	50 ; 52 ; 53 ; 54	52·01
Cobalt	Co	27	—	58·94
Columbium	Cb	41	—	92·91
Copper	Cu	29	63 ; 65	63·57
Dysprosium	Dy	66	161 ; 162 ; 163 ; 164	162·46
Erbium	Er	68	166 ; 167 ; 168 ; 170	167·64
Europium	Eu	63	151 ; 153	152·0
Fluorine	F	9	—	19·00
Gadolinium	Gd	64	155 ; 156 ; 157 ; 158 ; 160	157·3
Gallium	Ga	31	69 ; 71	69·72
Germanium	Ge	32	70 ; 72 ; 73 ; 74 ; 76	72·60
Gold	Au	79	—	197·2
Hafnium	Hf	72	176 ; 177 ; 178 ; 179 ; 180	178·6
Helium	He	2	—	4·002

	Symbol.	Atomic No.	Isotopes.	Atomic Wt.
Holmium	Ho	67	—	163·5
Hydrogen	H	1	1 ; 2 ; 3	1·0078
Indium	In	49	113 ; 115	114·76
Iodine	I	53	—	126·92
Iridium	Ir	77	191 ; 193	193·1
Iron	Fe	26	54 ; 56 ; 57 ; 58	55·84
Krypton	Kr	36	78 ; 80 ; 82 ; 83 ; 84 ; 86	83·7
Lanthanum	La	57	—	138·92
Lead	Pb	82	(203) ; 204 ; (205) ; 206 ; 207 ; 208 ; (209) ; (210)	207·22
Lithium	Li	3	6 ; 7	6·940
Lutecium	Lu	71	—	175·0
Magnesium	Mg	12	24 ; 25 ; 26	24·32
Manganese	Mn	25	—	54·93
Mercury	Hg	80	196 ; (197) ; 198 ; 199 ; 200 ; 201 ; 202 ; 203 ; 204	200·61
Molybdenum	Mo	42	92 ; 94 ; 95 ; 96 ; 97 ; 98 ; 100	96·0
Neodymium	Nd	60	142 ; 143 ; 144 ; 145 ; 146	144·27
Neon	Ne	10	20 ; 21 ; 22	20·183
Nickel	Ni	28	58 ; 60 ; (61) ; 62 ; 64	58·69
Nitrogen	N	7	14 ; 15	14·008
Osmium	Os	76	186 ; 187 ; 188 ; 189 ; 190 ; 192	191·5
Oxygen	O	8	16 ; 17 ; 18	16·000
Palladium	Pd	46	102 ; 104 ; 105 ; 106 ; 108 ; 110	106·7
Phosphorus	P	15	—	31·02
Platinum	Pt	78	192 ; 194 ; 195 ; 196 ; 198	195·23
Potassium	K	19	39 ; 40 ; 41	39·096
Praseodymium	Pr	59	—	140·92
Protactinium	Pa	91	—	231
Radium	Ra	88	—	226·05
Radon	Rn	86	—	222
Rhenium	Re	75	185 ; 187	186·31
Rhodium	Rh	45	—	102·91
Rubidium	Rb	37	85 ; 87	85·44
Ruthenium	Ru	44	96 ; (98) ; 99 ; 100 ; 101 ; 102 ; 104	101·7
Samarium	Sm	62	144 ; 147 ; 148 ; 149 ; 150 ; 152 ; 154	150·43
Scandium	Sc	21	—	45·10
Selenium	Se	34	74 ; 76 ; 77 ; 78 ; 80 ; 82	78·96
Silicon	Si	14	28 ; 29 ; 30	28·06
Silver	Ag	47	107 ; 109	107·880
Sodium	Na	11	—	22·997
Strontium	Sr	38	86 ; 87 ; 88	87·63
Sulphur	S	16	32 ; 33 ; 34	32·06
Tantalum	Ta	73	—	180·88
Tellurium	Te	52	122 ; 123 ; 124 ; 125 ; 126 ; 128 ; 130	127·61
Terbium	Tb	65	—	159·2
Thallium	Tl	81	203 ; 205	204·39
Thorium	Th	90	—	232·12
Thulium	Tm	69	—	169·4
Tin	Sn	50	112 ; 114 ; 115 ; 116 ; 117 ; 118 ; 119 ; 120 ; 122 ; 124	118·70
Titanium	Ti	22	46 ; 47 ; 48 ; 49 ; 50	47·90
Tungsten	W	74	182 ; 183 ; 184 ; 186	184·0
Uranium	U	92	235 ; 238	238·14
Vanadium	V	23	—	50·95
Xenon	Xe	54	124 ; 125 ; 126 ; 128 ; 129 ; 130 ; 131 ; 132 ; 134 ; 136	131·3
Ytterbium	Yb	70	171 ; 172 ; 173 ; 174 ; 176	173·04
Yttrium	Y	39	—	88·92
Zinc	Zn	30	64 ; 66 ; 67 ; 68 ; 70	65·38
Zirconium	Zr	40	90 ; 91 ; 92 ; 94 ; 96	91·22

Numbers in brackets are doubtful. **M. C.**

ATOMIC NUMBER *v.* Atomic Data and Atomic Structure.

ATOMIC STRUCTURE. The basis of the theory of atomic structure which is now generally accepted is due to Rutherford. The atom is believed to consist of a small positively charged nucleus surrounded by a number of electrons (*i.e.* unit charges of negative electricity). The total negative charges of the extra-nuclear electrons just neutralise the positive nuclear charge, with the result that the atom is normally electrically neutral. By adding one or more electrons to the extra-nuclear structure the electrical balance is upset, and a negative ion results. Similarly, if electrons are removed from the extra-nuclear structure, a positive ion is formed. The discussion of atomic structure may be conveniently subdivided by considering first the atomic nucleus, together with the nuclear phenomena of isotopy and radioactivity, and then the arrangement and properties of the extra-nuclear electrons.

The Atomic Nucleus.—The atomic nucleus is believed to be very small in relation to the atom itself. Atomic diameters are all of the order of 1 to 5×10^{-8} cm., and the nuclear diameter is 1/10,000 to 1/100,000 of this magnitude. This conclusion is based on experiments on the scattering of α-particles by matter. α-Particles are high-velocity helium nuclei with a positive charge of $2e$. The quantity e denotes the charge on the electron. It is the fundamental unit of positive or negative electricity, and has a numerical value of $4{\cdot}77\times10^{-10}$ electrostatic units. The α-particles are emitted during the disintegration of certain radioactive elements, and when they pass through matter (*e.g.* a very thin sheet of aluminium) some are deflected through small angles. A few, however, suffer much larger deflections of 90° or more from their original direction. This large deflection is attributed to the electrostatic repulsion set up when the positively charged α-particle happens to approach the positive atomic nucleus directly. Measurement of the frequency and magnitude of these large deflections leads to the conclusion that the positive electricity in the atom is concentrated in a region of the atom which offers a very small target area to the α-particle. This region is called the nucleus. The mass of the atom is also concentrated very largely in the nucleus, for the electron has only 1/1850 of the mass of the hydrogen atom, and the extra-nuclear structure contains only electrons.

A fundamental contribution to the study of the atomic nucleus was made in 1913 by Moseley (Phil. Mag. 1913, [vi], **26**, 1024 ; 1914, [vi], **27**, 703), as a result of the study of the X-ray spectra of a number of elements. The X-ray spectrum is produced most simply by bombarding an element or one of its compounds with fast electrons, when X-radiation of characteristic wave-length is emitted. X-rays are essentially the same as light waves, but the wave-length is shorter. Unlike the optical spectrum, the X-ray spectrum of an element is relatively very simple, and consists of a small number of groups of lines, known as the K, L, M . . . lines (*vide infra*). It was found by Moseley that there was an almost linear relationship between the values of, say, the greatest frequency (ν) in any one of these groups for a number of elements, and the square of the number assigned to the element in the sequence of increasing atomic weights from $H=1$ to $U=92$. The number of an element in this sequence is called the *atomic number* of the element (Z). Moseley's relationship is given by the equation $\nu=a\,(Z-b)^2$, where a and b are constants. The linear relationship between frequency and the square of the atomic number enabled several missing elements to be detected. There were gaps which corresponded with elements of atomic numbers 43, 61, 72, 75, 85, and 87. Of these six missing elements the first four have since been identified as masurium, illinium, hafnium, and rhenium, while there appears still to be some doubt as to the identity of 85 and 87.

The fundamental importance of Moseley's work lies in his suggestion that the atomic number of an element is identical with the positive charge on its atomic nucleus (the unit being again the electronic charge e). The atomic number must also be equal to the number of extra-nuclear electrons in the atom. A direct and independent determination of the nuclear charges for atoms of platinum, silver, and copper was made subsequently by Chadwick (Phil. Mag. 1920, [vi], **40**, 734) by measuring the deflection of α-particles in passing through foil of various metals, and resulted in a complete confirmation of their identity with the atomic numbers.

Radioactivity.—The nuclei of numerous heavy elements, and of a few of the lighter elements, disintegrate spontaneously, with the formation of new atomic nuclei, and the emission of particles of high energy, and of electromagnetic waves (γ rays). These phenomena are referred to collectively as radioactivity, and were first observed by Becquerel for uranium. Later they were observed for other elements, notably for radium (Pierre and Marie Curie). The particles emitted during radioactive disintegration are known as α-particles and β-rays, and their emission is accompanied by γ-radiation. The latter consists of waves of the same nature as light waves, but of very short wave-length (less than 10^{-8} cm.). The β-rays are negative electrons of high velocity. This is established by measurements of their deflection in electric and magnetic fields. The α-particles are helium atoms with a double positive charge and with high velocity. The α-particles must, on the Rutherford atomic theory, have come from the atomic nucleus, since this is the only part of the atom where there is any appreciable mass. They possess a definite velocity for a definite radioactive disintegration, and consequently have a definite range in a gas at a definite pressure (or in other media). The range is inversely proportional to the gas pressure, and decreases with increase in the molecular weight of the absorbing medium. Mica is often used to cut down the speed of α-particles. A flake weighing 1·5 mg. per sq. cm. is equivalent in stopping power to 1 cm. of air at 760 mm. pressure and 15°C.

The nuclear disintegration of radioactive substance follows the unimolecular law. This may be expressed by the relationship that the time for the initial activity to fall to half of its initial value (the *half-period*) is constant for a given disintegration process. The radioactive elements fall into three series, termed the uranium, thorium, and actinium series. In each of these series there is a sequence of radioactive disintegration taking place. Each element is being formed from the member of the series which precedes it. At the same time it is itself disintegrating. Under these conditions a radioactive equilibrium will be set up between the members of a series. The half-periods of different elements vary enormously, indicating a wide variation in nuclear stability. The data tabulated below refer to the uranium disintegration series, and serve to illustrate this point.

TABLE I.

	Atomic weight.	Atomic number.	Half period.	Radiation and range in air at N.T.P.
Uranium I	238	92	$4·4\times10^9$ Y	α 2·53 cm.
Uranium X_1	234	90	24·5 D	β, γ
Uranium X_2	234	91	1·17 M	β, γ
Uranium Z	234	91	6·69 H	β, γ
Uranium II	234	92	3×10^5 Y	α 2·96 cm.
Ionium	230	90	$8·3\times10^4$ Y	α 3·03 cm.
Radium	226	88	1,590 Y	α 3·21 cm.
Radon	222	86	3·82 D	α 3·91 cm.
Radium-A	218	84	3·05 M	α 4·48 cm.
Radium-B	214	82	26·8 M	β, γ
Radium-C	214	83	19·7 M	β, γ, or α
Radium-C_1	214	84	very short	α 6·60 cm.
Radium-C_2	210	81	1·32 M	β, γ
Radium-D	210	82	22 Y	β, γ
Radium-E	210	83	5·0 D	β, γ
Radium-F (Polonium) . . .	210	84	140 D	α 3·67 cm.
Radium-G (Lead)	206	82	—	—

(Y=years, D=days, H=hours, M=minutes.)

The emission of an α-particle from a radioactive nucleus decreases the atomic weight by four units and the atomic number by two units, while the loss of a β-particle leaves the atomic weight unchanged and increases the atomic number by unity, since the positive charge of the nucleus is increased by one unit.

The reason for the spontaneous decomposition of those radioactive atoms is not completely clear, although great progress has been made in this direction by the application of wave mechanics. Increase in the nuclear mass would be expected to lead to instability, but the wide range of half period values shows at once that the atomic mass is not the only factor controlling radioactive change. The problem is also complicated by the occurrence of radioactivity in the three elements potassium, rubidium, and samarium. Potassium and rubidium give rise to β- and γ-radiation, while samarium gives feeble α-ray activity, the range of the emitted α-particle being 1·1 cm. in air at N.T.P.

Artificial Transmutation.—The disintegration of atomic nuclei by bombardment with α-particles was first observed by Rutherford (J.C.S. 1922, **121**, 400). This disintegration is a direct result of a close collision between the α-particle and the nucleus of the atom bombarded, and in most cases it results in the ejection of a *proton* (*i.e.* a positively charged hydrogen atom). The latter can have a range of up to almost 100 cm. in air at N.T.P., depending on the element bombarded and on the direction of emission. Disintegrations of this type have been observed in a number of the lighter elements (*e.g.* in nitrogen), and the paths of the ejected particle and of the recoil atom have actually been photographed, by making use of the property of the ions formed in the tracks of such particles of acting as nuclei for the condensation of fog particles (Wilson cloud chamber). Nuclear disintegration can also be produced by bombardment with protons produced in an electric discharge, and accelerated to a sufficiently high velocity by means of an electric field. The study of the action of α-rays on beryllium has revealed the existence of another product of nuclear disintegration—the *neutron*. This is a particle which is almost identical in mass with the hydrogen atom, but which has no electrical charge. A further disintegration product is the *positive electron* or *positron*. This, as the name implies, is a particle with a mass equal to that of the electron, but with a unit positive charge ($+e$).

The actual structure of atomic nuclei has been the subject of considerable speculation. Such information as we have is derived from considerations such as the energy relations of γ-rays from radioactive disintegrations. Rutherford has suggested that the nucleus contains a central core, together with a number of satellite α-particles in quantised orbits (*cf.* Proc. Roy. Soc. 1932, A, **136**, 735). The whole question is, however, still somewhat uncertain, and awaits the application both of fresh experimental work and of modern quantum theory.

Induced Radioactivity.—A new chapter in the study of atomic nuclei was opened up in 1934 by Mme. Curie-Joliot and M. Joliot (Compt. rend. 1934, **198**, 254) in the course of work on the bombardment of some of the lighter elements with α-particles. These workers found that when an element such as boron was exposed to a source of α-particles it acquired an "induced" radioactivity. Even when removed completely from the source of α-particles it was able for some time to emit high-velocity particles capable of producing discharges in a Geiger-Müller counter. The irradiated boron had, in fact, all the characteristics of a radioactive element. Its activity took a definite and characteristic time to decay to half of its initial value. When boron nitride was exposed to α-particles and the product was dissolved in sodium hydroxide solution, the activity was found to be carried away with the ammonia evolved. The bombardment had produced an isotope of nitrogen which was unstable, and which was disintegrating into a carbon isotope according to the scheme :

$$\mathrm{B}_5^{10} + \mathrm{He}_2^4 \rightarrow \mathrm{N}_7^{13} + n_0^1$$

$$\mathrm{N}_7^{13} \rightarrow \mathrm{C}_6^{13} + e+$$

In this scheme the upper and lower index numbers denote respectively the mass and nuclear charge (or atomic number) of the particular atom. The first stage involves the production of a neutron (first identified by Chadwick in 1932). The second stage is the one responsible for the induced radioactivity, the actual particle which affects the counter being in this case a positron. The half period of the nitrogen isotope N_7^{13} was found to be 14 mins. Similar experiments were carried out with a number of the lighter elements, including aluminium which gave an active isotope of phosphorus as the initial product, and magnesium, which gave an active isotope of silicon. The names radio-nitrogen, radio-phosphorus, and radio-silicon were proposed for these new elements. It should be emphasised that the quantity of active material formed was, in these early experiments in particular, exceedingly small, and that the detection of the phenomenon is due entirely to the very delicate methods available in the study of radioactivity. Bombardment with α-particles is subject to the limitation that the repulsive forces between the α-particles and the nucleus of the bombarded element increase greatly as soon as the atomic number of the latter becomes fairly large. Consequently, an α-particle has very little chance of close approach to the nucleus of a heavy atom. This disability is completely removed when neutrons (produced from beryllium) are used for the bombardment, and their application has added greatly to the list of elements known to exhibit the phenomenon of artificial radioactivity (*cf.* Fermi *et alia*, Proc. Roy. Soc. 1934, A, **146**, 483 ; 1935, A, **149**, 522). As in the case in which the α-particle was used, the neutron first converts the nucleus with which it collides into a new and unstable species. The latter then disintegrates spontaneously. In the case of aluminium, for example, one of the processes taking place is believed to be :

$$\mathrm{Al}_{13}^{27} + n_0^1 \rightarrow \mathrm{Na}_{11}^{24} + \mathrm{He}_2^4$$

$$\mathrm{Na}_{11}^{24} \rightarrow \mathrm{Mg}_{12}^{24} + e$$

The activity in this case is due to emission of an electron, and in this respect is parallel to the β-ray activity of naturally radioactive elements. By the use of the neutron method over sixty elements have now been found to yield products which exhibit induced radioactivity. In a number of cases (*e.g.* for aluminium) more than one half-period has been observed for the same element. The subject is still being studied in a number of laboratories, and has already yielded results of the utmost importance in the study of the atomic nucleus.

Isotopes.—The early study of radioactivity revealed the very striking fact that certain elements with different radioactive characteristics could not be separated chemically. Thorium and ionium are a case in point. Such elements were called by Soddy *isotopes*. The majority of the chemical elements are now known to occur as isotopes, and the term may be defined as denoting elements the atoms of which have the same nuclear charge (or atomic number) but different nuclear constitution and atomic weight. The identity of the nuclear charges implies that two isotopic elements will have the same number of extra-nuclear electrons. Hence two isotopic elements will, in general, have almost identical chemical properties, for it is on these electrons, and especially on those in the outer regions of the atom, that the chemical properties depend. The difference between the atomic nuclei of two isotopes is in their masses. If the proton be taken as the nuclear unit, the nucleus of one of two isotopes might be considered as containing more protons than the other, together with a sufficient number of electrons to give the isotopes the same nuclear charge or atomic number. Alternatively, neutrons may exist in the nucleus.

Isotopes of non-radioactive elements were first studied by J. J. Thomson by the positive ray parabola method (*cf.* J. J. Thomson, "Rays of Positive Electricity," 1913). More recently, great refinements have been introduced by Aston and others, and precision determinations of the abundances and relative weights of the isotopes of most of the elements have now been made. The Aston mass spectrograph employs a combination of a magnetic and an electric field to sort out a beam of positive ions of the element examined, so that all particles with a given ratio of charge to mass are brought to a focus and can be recorded photographically. The study of atomic and molecular spectra also serves to detect isotopes and to estimate their relative abundance. This method was used in the case of the oxygen isotopes O^{16}, O^{17}, and O^{18}, and for the carbon isotopes C^{12} and C^{13}. In general, it may be stated that isotopes will show a difference in any property which depends on atomic mass, and such differences have been employed in certain cases to effect a partial separation. The neon isotopes Ne^{20} and Ne^{22}, for example, have been almost completely separated by a process of fractional diffusion through porous material, and, less completely, by fractional distillation of liquid neon. Similarly, a partial separation of the mercury isotopes has been achieved by a process of fractional evaporation at low pressures. Only in the case of the recently discovered hydrogen isotope of mass 2 (deuterium) is there any considerable difference in the chemical properties of the isotopic species.

The atomic weight of an element as measured by chemical methods is a mean value, determined by the masses of the isotopes of the element in question, and their relative abundance. The discovery of isotopes, together with the conception of atomic numbers, has cleared up the anomaly presented by the atomic weights of the elements argon and potassium, cobalt and nickel, and tellurium and iodine. Following the order of chemical atomic weights, these pairs of elements fall in the wrong order in the periodic table, and in the sequence of atomic numbers. This is entirely due to the relative abundance of their isotopes. Argon, for example, has a chemical atomic weight of 39·94, while potassium, which must follow it in the periodic table, has a lower atomic weight (39·10). This arises from the fact that argon contains 99% A^{40} and 1% of A^{36}, whereas potassium contains 95% of K^{39} and only 5% of K^{41}.

The Extra-Nuclear Structure.—The electrons which make up the extra-nuclear structure may, from many chemical points of view, be regarded as very small units each with an electrical charge equal to $-e$. These electrons are held in position by the electrostatic attraction of the positive atomic nucleus, and they are arranged for the various elements in definite orbits about the nucleus. The basis of our present conception of electron arrangement is due to Bohr, who postulated (initially for the simple case of the hydrogen atom with one electron) that only certain electron orbits are possible. Such orbits were termed *stationary states*. The angular momentum associated with each possible orbit was taken on his model to be an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant, which has a numerical value of $6{\cdot}55\times10^{-27}$ erg-sec. The transition of an electron from one orbit of energy E′ to another of energy E″ will result in the emission or absorption of radiation, according to whether E′ is greater or less than E″. The frequency of this radiation (ν) is given by the relation

$$E'-E''=h\nu.$$

The possible electron orbits were classified by a series of *quantum numbers*. The energy (W_n) of an electron in a hydrogen-like atom with one electron, but with nuclear charge $+Ze$ is given closely by the expression :

$$W_n=\frac{-2\pi^2Z^2e^4\mu}{h^2}\left(\frac{1}{n^2}\right)$$

where n, which can have the values 1, 2, 3, 4 . . ., is called the *principal quantum number*, Z denotes the nuclear charge, h is Planck's constant, and e and μ are the electronic charge and mass respectively. When n is unity the energy is least and the corresponding orbit is the one nearest to the nucleus. In atoms with more than one orbital electron the energy relations are more complex, but it is still possible to assign to each electron an integral principal quantum number n.

Electrons with the principal quantum number of unity are called K electrons. The maximum number of such electrons is 2, there being 1 in the neutral hydrogen atom and 2 in the neutral helium atom. Electrons with principal quantum numbers of 2, 3, 4 . . . are termed L, M, N . . . electrons respectively. They occur, roughly speaking, in shells which become further removed from the nucleus as n increases. The atoms do not, however, become on the average larger as the number of electrons increases. This is because the increased nuclear charge makes the whole system more compact; *e.g.* as Z increases the mean radius of the K shell decreases. The distribution of electrons in the rare gases is shown in the following table :

TABLE II.

	Atomic number.	$n=$ 1 K	2 L	3 M	4 N	5 O	6 P
Helium . .	2	2					
Neon . . .	10	2	8				
Argon . . .	18	2	8	8			
Krypton . .	36	2	8	18	8		
Xenon . .	54	2	8	18	18	8	
Radon . .	86	2	8	18	32	18	8

The study of the optical and X-ray spectra of the elements shows that the principal quantum number alone does not suffice to account for all the electron orbits. Each state of principal quantum number n is split into n sublevels, which are differentiated by a second quantum number l, the *subsidiary* or *azimuthal quantum number*. The physical significance of l is that $\frac{l(l+1)h^2}{4\pi^2}$ is equal to the square of the orbital angular momentum of the electron in its stationary state. When the principal quantum number is n, l can have the values 0, 1, 2, 3, ... ($n-1$). Such electrons are called *s*, *p*, *d*, and *f* . . . electrons respectively. Thus, for example, a 4*d* electron is one which is situated in the fourth quantum group (principal quantum number=4), and which has, in addition, $l=2$.

It is necessary to introduce two further quantum numbers, the ***magnetic quantum number*** m and the ***spin quantum number*** s, in order to account for spectroscopic phenomena. The magnetic quantum number expresses (roughly) the fact that the plane of an electron orbit can only take up certain orientations with respect to the direction of an applied magnetic field. The energy corresponding to each of these orientations will be different. The possible values of m are $-l, (-l+1) \ldots\ldots -1, 0 \ldots (l-1), (l)$, the number of such values being thus $(2l+1)$. For an s electron this is 1, for a p electron it is 3, for a d electron it is 5, and for an f electron it is 7. The electron is also capable of rotating about its own axis, in addition to executing its orbital motion. This "*spin*" is also quantised, and is associated with the spin quantum number s which has the values $\pm 1/2$. One further link is needed before the number of electrons in each electron shell can be determined. This is the *Pauli exclusion principle*, according to which no two electrons in a given atom can have the same four quantum numbers, n, m, l, and s.

In the K group ($n=1$) there is only one possible value of l ($l=0$). For $l=0$, the maximum number of values of $m=2l+1=1$, and for this value of m the spin quantum number (s) is $\pm 1/2$. There are therefore two electrons at the most in the K shell. In the L shell ($n=2$), l can have the values 0 or 1. Two orbits are possible for $l=0$, as already shown. For $l=1$, the number of values of $m=2l+1=3$, and for each of those three values of m, s can have the values $\pm 1/2$. There will therefore be $(2+6)=8$ possible orbits in the L shell. In the rare gas neon, which has 10 electrons, the K and L orbits are completely filled. When $n=3$ (M shell), l can be 0, 1, or 2. When $l=0$ and 1, 8 orbits are possible, as already shown. When $l=2$, m can have 5 values ($=2l+1$), and for each of these the spin quantum number can be $\pm 1/2$. There is therefore a maximum of 18 possible electron orbits in the third (M) electron shell. For $n=4$, l can have the values 0, 1, 2, and 3. When $l=3$, $m=7$, and the maximum number of orbits is equal to 32.

The use of these four quantum numbers gives at once a real physical basis to the characteristic arrangement of the periodic table, in which the periods contain successively 2, 8, 8, 18, 18, and 32 elements. It is possible, from the study of line spectra, to state with some certainty the quantum numbers of all the electrons for the chemical elements. Table III shows such an arrangement in which the principal and subsidiary quantum numbers are specified. In this scheme each element can be considered as formed from the one preceding it by adding unit positive charge to the nucleus, and one electron to the extra-nuclear structure. This new electron does not necessarily go into the allowed orbit with the lowest quantum number. For potassium and calcium, for example, it will be seen that the added electrons occupy one and two $4s$ orbits respectively, though orbits of principal quantum number 3 are still vacant. With the next element, scandium, the added electron does, indeed, go into the $3d$ orbit. The reason for this apparent anomaly is that the normal state of an atom is one in which the electrons are bound as tightly as possible, and with potassium and calcium the energy of the added electron is less when it is in a $4s$ orbit than when it is in a $3d$ orbit. A similar anomaly occurs with other elements of greater atomic number.

In the elements between scandium and nickel the number of electrons in the M shell ($n=3$) is increased up to 16, while in the element beyond nickel (copper) the M shell is full (18 electrons). These elements in which the inner atomic shell is being completed, while the outer shell of electrons (which largely controls the valency) remains unchanged, correspond with the first group of *transition elements* in the periodic system, extending from scandium to nickel.

Between copper and krypton the s and p orbits of the outer shell ($n=4$) are being built up to their respective maxima of 2 and 6 electrons. The next two elements, rubidium and strontium, have respectively 1 and 2 s electrons in the O shell ($n=5$), but the next 8 elements are again transition elements, and correspond with the building up of the d orbits in the N shell from 1 to 10. The added electrons for the next 8 elements complete the $5s$ and $5p$ orbits of the O shell, which are full in the rare gas xenon. Cæsium and barium, the next two elements, have respectively 1 and 2 $6s$ electrons. In the 14 rare earth elements (cerium to lutecium) which follow, inner building again occurs, this time with increase in the number of electrons in the N shell up to the maximum of 32, by completion of the vacant $4f$ orbits. The number of electrons in the outermost shell remains constant in the rare earths, and since this number determines the valency, the rare earth elements as a group show close chemical similarity. Following the rare earths is a further group of transition elements (hafnium to platinum) for which the $5d$ orbits of the O shell are being completed. In the elements from gold to radium the added electrons go to the outer shells. Finally, the four elements actinium, thorium, protactinium, and uranium form a further incomplete group of transition elements in which the $6d$ orbits are beginning to be filled.

There is no doubt that the above scheme represents a substantially correct picture of the arrangement of the electrons in the chemical atom. It is the electrons in the outermost shell of an atom which can interact with the electrons of other atoms. Accordingly the number of such electrons will govern the chemical valency of the element in question. All of the rare gases have a completed outer subshell of 8 electrons. They are chemically inert and have high ionisation potentials. This structure with a completed outer octet of electrons is a particularly stable arrangement, and the electronic theory of valency is based on the idea that molecule formation occurs in such a way as to give each atom in the molecule an inert gas structure.

Excited Atoms and Spectra.—The statements in the preceding section refer to atoms in their normal states. If energy is supplied to an atom (*e.g.* in the course of a chemical reaction or in an electrical discharge), the atom may pass

TABLE III.—THE ELECTRON GROUPS OF THE PERIODIC TABLE.

This table is based on the Table of Electron Configurations given in " The Optical Basis of the Theory of Valency," by R. de L. Kronig, Cambridge University Press, 1935.

		K	L		M			N			
n =		1	2		3			4			
		s	s	p	s	p	d	s	p	d	f
1	H	1									
2	He	2									
3	Li	2	1								
4	Be	2	2								
5	B	2	2	1							
6	C	2	2	2							
7	N	2	2	3							
8	O	2	2	4							
9	F	2	2	5							
10	Ne	2	2	6							
11	Na	2	2	6	1						
12	Mg	2	2	6	2						
13	Al	2	2	6	2	1					
14	Si	2	2	6	2	2					
15	P	2	2	6	2	3					
16	S	2	2	6	2	4					
17	Cl	2	2	6	2	5					
18	A	2	2	6	2	6					
19	K	2	2	6	2	6		1			
20	Ca	2	2	6	2	6		2			
21	Sc	2	2	6	2	6	1	2			
22	Ti	2	2	6	2	6	2	2			
23	V	2	2	6	2	6	3	2			
24	Cr	2	2	6	2	6	5	1			
25	Mn	2	2	6	2	6	5	2			
26	Fe	2	2	6	2	6	6	2			
27	Co	2	2	6	2	6	7	2			
28	Ni	2	2	6	2	6	8	2			
29	Cu	2	2	6	2	6	10	1			
30	Zn	2	2	6	2	6	10	2			
31	Ga	2	2	6	2	6	10	2	1		
32	Ge	2	2	6	2	6	10	2	2		
33	As	2	2	6	2	6	10	2	3		
34	Se	2	2	6	2	6	10	2	4		
35	Br	2	2	6	2	6	10	2	5		
36	Kr	2	2	6	2	6	10	2	6		

		K	L	M	N				O				P	
n =		1	2	3	4				5				6	
					s	p	d	f	s	p	d	f	s	p
37	Rb	2	8	18	2	6			1					
38	Sr	2	8	18	2	6			2					
39	Y	2	8	18	2	6	1		2					
40	Zr	2	8	18	2	6	2		2					
41	Nb	2	8	18	2	6	4		1					
42	Mo	2	8	18	2	6	5		1					
43	Ma	2	8	18	2	6	6		1					
44	Ru	2	8	18	2	6	7		1					
45	Rh	2	8	18	2	6	8		1					
46	Pd	2	8	18	2	6	10							
47	Ag	2	8	18	2	6	10		1					
48	Cd	2	8	18	2	6	10		2					
49	In	2	8	18	2	6	10		2	1				
50	Sn	2	8	18	2	6	10		2	2				
51	Sb	2	8	18	2	6	10		2	3				
52	Te	2	8	18	2	6	10		2	4				
53	I	2	8	18	2	6	10		2	5				
54	X	2	8	18	2	6	10		2	6				
55	Cs	2	8	18	2	6	10		2	6			1	
56	Ba	2	8	18	2	6	10		2	6			2	
57	La	2	8	18	2	6	10		2	6	1		2	
58	Ce	2	8	18	2	6	10	1	2	6	1		2	
59	Pr	2	8	18	2	6	10	2	2	6	1		2	
60	Nd	2	8	18	2	6	10	3	2	6	1		2	
61	Il	2	8	18	2	6	10	4	2	6	1		2	
62	Sm	2	8	18	2	6	10	5	2	6	1		2	
63	Eu	2	8	18	2	6	10	6	2	6	1		2	
64	Gd	2	8	18	2	6	10	7	2	6	1		2	
65	Tb	2	8	18	2	6	10	8	2	6	1		2	
66	Dy	2	8	18	2	6	10	9	2	6	1		2	
67	Ho	2	8	18	2	6	10	10	2	6	1		2	
68	Er	2	8	18	2	6	10	11	2	6	1		2	
69	Tm	2	8	18	2	6	10	12	2	6	1		2	
70	Yb	2	8	18	2	6	10	13	2	6	1		2	
71	Lu	2	8	18	2	6	10	14	2	6	1		2	

		K	L	M	N	O			P			Q
n =		1	2	3	4	5			6			7
						s	p	d	s	p	d	s
72	Hf	2	8	18	32	2	6	2	2			
73	Ta	2	8	18	32	2	6	3	2			
74	W	2	8	18	32	2	6	4	2			
75	Re	2	8	18	32	2	6	5	2			
76	Os	2	8	18	32	2	6	6	2			
77	Ir	2	8	18	32	2	6	7	2			
78	Pt	2	8	18	32	2	6	9	1			
79	Au	2	8	18	32	2	6	10	1			
80	Hg	2	8	18	32	2	6	10	2			
81	Tl	2	8	18	32	2	6	10	2	1		
82	Pb	2	8	18	32	2	6	10	2	2		
83	Bi	2	8	18	32	2	6	10	2	3		
84	Po	2	8	18	32	2	6	10	2	4		
85	—	2	8	18	32	2	6	10	2	5		
86	Rn	2	8	18	32	2	6	10	2	6		
87	—	2	8	18	32	2	6	10	2	6		1
88	Ra	2	8	18	32	2	6	10	2	6		2
89	Ac	2	8	18	32	2	6	10	2	6	1	2
90	Th	2	8	18	32	2	6	10	2	6	2	2
91	Pa	2	8	18	32	2	6	10	2	6	3	2
92	U	2	8	18	32	2	6	10	2	6	4	2

into an *excited state.* In this state energy has been absorbed by the atom, and one or more of the electrons has been removed to an outer orbit. The optical spectrum of an atom is emitted or absorbed when the outer electrons move from one set of orbits to another. In the extreme case of complete removal of an electron from an atom the latter is said to be *ionised,* forming a positive ion. A negative ion results if an atom gains an electron. The X-ray spectrum of an element arises in a rearrangement of the inner (particularly K and L) electrons. If one of these electrons is taken through the occupied intermediate L, M . . . shells to an outer unoccupied valency orbit, or is removed from the atom completely, the vacant space left in the inner shell may be filled by an electron jumping into it from one of the intermediate orbits. The energy thus made available will be radiated as X-radiation of frequency governed by the quantum relationships. H. J. E.

ATONIN *v.* ASPIRIN.

ATOPHAN. Trade name for 2-phenylquinoline-4-carboxylic acid, 2-phenylcinchonic acid. *v.* QUINOLINE.

ATOQUINOL. Trade name for allyl-2-phenylcinchonate, m.p. 30°. Antirheumatic.

ATOXYL, Arsamin, Soamin = sodium *p*-arsanilate (*v.* ARSENICALS, ORGANIC).

ATRACTYLOL *v.* EUDESMOL.

ATRANORIN *v.* LICHENS.

ATROLACTINIC ACID (α-phenyl-α-hydroxypropionic acid, $CH_3{\cdot}CPh(OH)COOH$ prepared by the hydrolysis of acetophenone cyanhydrin, m.p. 93°–94° (Spiegel, Ber. 1881, **14**, 1353 ; Tiemann and Köhler, *ibid.* 1980).

ATROPAMINE=*apo*-Atropine (*v*, SOLANACEOUS ALKALOIDS).

ATROSCINE *v.* SOLANACEOUS ALKALOIDS.

ATTAR OF ROSES (*Otto de Rose*). The oil distilled from the fresh flowers of the damask rose, *Rosa damascena* Linn. (N.O. Rosaceæ), which is chiefly cultivated in Bulgaria. It is a pale yellow semicrystalline mass at ordinary temperatures, liquefying at about 23°C. It forms a turbid mixture with alcohol, due to the presence of a mixture of solid hydrocarbons known as *stearoptene* which is practically odourless. French otto of roses is distilled from the flowers of *Rosa centifolia* and other species, the product differing in odour and properties from the Bulgarian oil. The chief adulterants of the latter oil are geraniol, citronellol and phenyl-ethyl alcohol, all of which raise the specific gravity and lower the melting-point. Paraffin wax, spermaceti and alcohol are sometimes added to compensate for these additions and it is therefore necessary to examine the stearoptene. The addition of geraniol and citronellol is difficult to detect as these are natural constituents of the oil and the sense of smell is one of the most useful means for the expert to assess the value of a particular oil.

Characters.—Sp.gr. (30°/15·5°), 0·852 to 0·862, opt. rot. −2 to −4 ; n_{25} 1·458 to 1·465.

Constituents.—Geraniol, citronellol, nerol, farnesol, phenyl-ethyl alcohol and stearoptene. The proportion of total alcohols is from 70–75%, of which citronellol constitutes from one-third to one-half of the liquid portion of the oil. The proportion of citronellol may be approximately determined by heating with concentrated formic acid, which largely but not entirely destroys the geraniol and forms citronellol formate.

The stearoptene consists of two or more paraffin hydrocarbons melting at 22° and 40° respectively. The mixture melts at 32°–37°. The stearoptene of the tea rose melts at 14°, and French otto of roses contains this liquid stearoptene. C. T. B.

ATYROSYL. Syn. for Asyphil.

AUBEPINE *v.* ANISALDEHYDE and PERFUMES, SYNTHETIC.

AUCUBIGENIN *v.* AUCUBIN.

AUCUBIN. The characteristic glycoside of the spotted laurel (*Aucuba japonica,* L.), which causes the leaf to go black when injured or exposed to organic vapours, is hydrolysed to glucose and *aucubigenin.* It appears to be generally distributed and is sometimes called *Rhinanthin.* The constitution of the aglucone is unknown. Bergmann and Michaelis (Ber. 1927, **60** [B], 935) give to aucubin the composition $C_{15}H_{22}O_9$ or $C_{15}H_{24}O_9$; this latter is preferred by Kariyone and Kondo (J. Pharm. Soc. Japan, 1928, **48**, 90). Aucubin takes up 4 atoms of hydrogen on hydrogenation and then no longer gives dark decomposition products with acids or emulsin. The Japanese investigators find it to take up 4 mols. of hydrogen, of which 2 are required by the double bond, 1 for reduction of an hydroxyl and 1 for the hydrolysis. Under other conditions 3 mols. of hydrogen are taken up without splitting off the glucose. E. F. A.

AUGELITE. Basic aluminium phosphate, $AlPO_4{\cdot}Al(OH)_3$, occurring as colourless monoclinic crystals with cleavages in three directions, and much resembling baryte in appearance. It was first found in 1868 in an iron mine at Westanå, Sweden, and afterwards at several places in silver-tin mines in Bolivia (Prior and Spencer, Min. Mag. 1895, **11**, 16 ; Spencer, *ibid.* 1898, **12**, 1 ; *ibid.* 1907, **14**, 323). More recently it has been found in the andalusite mine on White Mountain, Mono County, California (D. M. Lemmon, Amer. Min. 1935, **20**, 664). L. J. S.

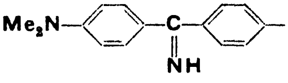
AUGITE *v.* BASALT.

AURACIN G *v.* ACRIDINE.

AURAMINE. The hydrochloride of *pp′*-bisdimethylamino-benzophenoneimine,

$$C_{17}H_{21}N_3{\cdot}HCl{\cdot}H_2O,$$

is the most important dyestuff of the diphenylmethane series. The term auramine should strictly be given to the free base,



but it is customary to call this *auramine base* and to apply the name auramine to the hydrochloride, which is the commercial dyestuff (*cf.* Fehrmann, Ber. 1887, **20**, 2846 ; Graebe, *ibid.* 3263). The structure of the hydrochloride and similar salts is discussed below. The pure dyestuff is also called *Auramine O. Auramine I,* *II*, and *III* are varieties diluted with dextrin. *Auramine G* is a compound of similar structure, described later.

Preparation.—(1) Auramine is now prepared by the following method (Geigy, G.P. 53614 of 1889 ; Friedländer,[1] **2**, 60). 12·7 kg. of tetramethyldiaminodiphenylmethane,

$$Me_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe_2,$$

with 3·2 kg. of sulphur are heated in a closed vessel fitted with a stirrer in an oil bath until the sulphur goes into solution. A mixture of 120 kg. of salt and 7 kg. of finely pulverised ammonium chloride, previously heated to 140°, is then added. The temperature of the oil bath is raised to 175° and a fairly vigorous stream of dry ammonia gas is passed into the vessel for 7 hours under an excess pressure of ¼ atmosphere. The escaping ammonia is freed from hydrogen sulphide by means of caustic soda, dried, and recirculated. The reaction product, a brownish-yellow powder, is freed from salt with cold water ; the dyestuff is extracted with warm water, the solution filtered, and the dye precipitated by the addition of the salt solution obtained in the first washing.

Various modifications of this method have been patented. Quinone, nitrobenzene, and other oxidising agents may be used in place of sulphur (B.A.S.F., G.P., 70908 of 1893, Friedländer, **3**, 88). Tetramethyldiaminodiphenylpropane, $Me_2N{\cdot}C_6H_4{\cdot}CMe_2{\cdot}C_6H_4{\cdot}NMe_2$, may be used in place of tetramethyldiaminodiphenylmethane (B.A.S.F., G.P. 71320 of 1893, Friedländer, **3**, 89). For preparations from Michler's hydrol,

$$Me_2N{\cdot}C_6H_4{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NMe_2,$$

see G.P. 58277 and 70908.

(2) The original method of preparation (Caro and Kern, 1883) was from Michler's ketone (tetramethyldiaminobenzophenone), two modifications being used : (*a*) The ketone dissolved in an indifferent solvent was converted into a chloro-derivative by the action of phosphorus trichloride or oxychloride (B.A.S.F., G.P. 27789 of 1883); this yielded auramine on treatment with ammonia (B.A.S.F., G.P. 29060 of 1884). (*b*) The ketone was heated with an ammonium salt (*e.g.* the chloride) and zinc chloride to 200° (G.P. 29060).

(3) Guyot's synthesis is of interest in confirming the position of the imino-group on the central carbon atom (Compt. rend. 1907, **144**, 1219 ; Bull. Soc. chim. 1907 [iv], **1**, 937 ; J.S.C.I. 1907, 603 ; 1908, 679). In this α-amino-*pp'*-bisdimethylaminodiphenyl acetic acid $(Me_2N{\cdot}C_6H_4)_2C(NH_2){\cdot}CO_2H$ was oxidised in dilute alkaline solution with cold dilute aqueous potassium ferricyanide, auramine being formed quantitatively.

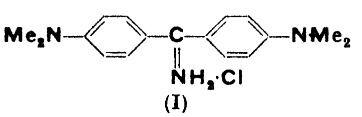
Auramine base ($C_{17}H_{21}N_3$) is prepared from the pure hydrochloride by treatment with ammonia (Fehrmann, Ber. 1887, **20**, 2849) or with an excess of caustic soda, the base being extracted with benzene (Semper, Annalen, 1911, **381**, 247).

Properties.—Auramine (hydrochloride) crystallises from water in yellow scales, apparently six-sided tablets, and from alcohol in golden-yellow scales, m.p. 267°. It is sparingly soluble in cold water, more soluble in alcohol. The aqueous solution decomposes at *ca.* 70° into ammonia and tetramethyldiaminobenzophenone. A similar reaction occurs in dilute acid solution even in the cold. Increase in temperature and acidity assists this hydrolysis (Holmes and Darling, J. Amer. Chem. Soc. 1924, **46**, 2343). Auramine base crystallises from alcohol in colourless plates, m.p. 136° ; it is insoluble in water and soluble in 96% alcohol and ether to the extent of 7 and 2·3% respectively. The base becomes yellow on standing in air containing carbon dioxide ; and the colourless solution in benzene becomes yellow on the addition of alcohol.

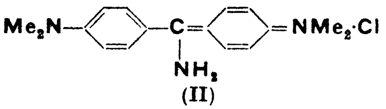
For the absorption spectra of the base and salts, *see* Graebe, Ber. 1887, **20**, 3265 ; Grandmougin and Favre-Ambrumyan, Ber. 1914, **47**, 2127 ; Massol and Faucon, Bull. Soc. chim. 1913 [iv], **13**, 702 ; Semper, *l.c.* For measurements of electrical conductivity of the salts, *see* Hantzsch and Osswald, Ber. 1900, **33**, 297 ; Sidgwick and Moore, Z. physikal. Chem. 1907, **58**, 393 ; Semper, *l.c.* Auramine base is slowly reduced in alcoholic solution by sodium amalgam to *leucauramine*, $C_{17}H_{23}N_3$, a colourless base, m.p. 135°. A similar reduction is effected by zinc and hydrochloric acid. The leuco-base gives an intense blue solution in acetic acid owing to its conversion into ammonia and Michler's hydrol. Other reactions of auramine are given below under the section on substituted auramines.

Uses.—Auramine dyes cotton mordanted with tannin and tartar emetic in pure yellow shades of moderate fastness from an aqueous solution at 60°–70°. Wool and silk are dyed direct from a neutral bath or one containing a little acetic acid. The dye is mainly used on tannin-mordanted cotton, particularly with other basic dyes ; also for dyeing paper, leather, rayon, etc. It is used as an antiseptic under the name *Pyoktanin* ; for the physiological action, *see* Führer, Ber. 1906, **39**, 2437.

Structure of Auramine (Hydrochloride).—The structure of auramine base follows with certainty from the methods of preparation and the hydrolysis of the leuco-base to Michler's ketone and ammonia. Two formulæ have, however, been proposed for the dye itself :



(I)

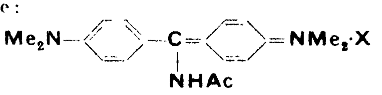


(II)

The first, proposed by Graebe and by Fehrmann (*l.c.*), represents the dye as being formed by simple addition of hydrogen chloride to the imino-group ; the second, due to Stock (J. pr. Chem. 1893 [ii], **47**, 401 ; Ber. 1900, **33**, 318), involves a benzenoid → quinonoid change of one nucleus, and salt-formation on a dimethylamino group. The main evidence at first adduced for formula (I) was the resemblance between auramine and the yellow salts of other benzophenoneimines, which could not exist in quinonoid modifications, *e.g.* $Ph_2C=NPh$ (Graebe, Ber. 1899, **32**, 1681 ; 1902, **35**, 2615). Against (I) it has been urged that the imino-group is a weak chromophore and that the formation of a coloured salt from a colourless base recalls the behaviour of the triphenylmethane series of dyes, in which the salts are undoubtedly quinonoid. Evidence apparently in favour of (II) came from the physical work of Hantzsch and Osswald (*l.c.*), but this was shown to be inconclusive by Semper (*l.c.*). Semper also showed that the *N*-acetyl derivative of auramine on treatment with acids, metallic halides, or alkyl halides yielded unstable blue-violet or green-blue salts. These differed completely in properties, including absorption spectra, from the salts of auramine base and its alkyl or aryl derivatives, but resembled the salts of Michler's hydrol, which are undoubtedly quinonoid. These salts must therefore be of the type :

---

[1] "Fortschritte der Theerfarben Fabrikation," Friedländer, Berlin, Springer, 1887–1930.



whereas auramine itself must have formula (I). This is supported by the spectrographic work of Grandmougin and Favre-Ambrumyan (*l.c.*). For further theoretical discussion of the structure of auramine, *see* Madelung, J. pr. Chem. 1926 [ii], **114**, 1.

Other Salts of Auramine Base.—The following have been described: *Hydriodide*, $C_{17}H_{21}N_3\cdot HI$, yellow powder, m.p. 267°–268° (Graebe, Ber. 1887, **20**, 3265) ; *propionate*, orange leaflets ; *palmitate*, $C_{17}H_{21}N_3\cdot C_{16}H_{32}O_2$, orange powder, m.p. 57° ; *stearate*, m.p. 68° (Gnehm and Rötheli, Z. angew. Chem. 1898, **11**, 487).

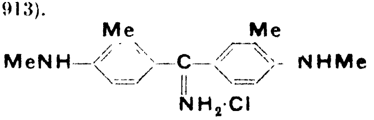
Substituted Auramines.—N-*Methyl auramine*, $(Me_2N\cdot C_6H_4)_2\cdot C : NMe$. The hydriodide, $C_{18}H_{23}N_3\cdot HI$, is formed by the action of methyl iodide on auramine base (Graebe, Ber. 1902, **35**, 2618), and the methosulphate, m.p. 225°, by the action of dimethyl sulphate on auramine base in ether (Zohlen, J. pr. Chem. 1902 [ii], **66**, 387). The free base, pale yellow, m.p. 133°, is liberated from these salts by the action of alkali. The salts are bright yellow ; a considerable number have been described by Graebe and by Zohlen (*l.c.*).

N-*Ethyl Auramine*, $(Me_2N\cdot C_6H_4)_2\cdot C : NEt$. Prepared from auramine base, ethyl iodide, and zinc oxide (G.P. 136616), m.p. 130°–131°. The salts dye tannin-mordanted cotton a pure yellow.

N-*Phenyl Auramine*, $(Me_2N\cdot C_6H_4)_2\cdot C : NPh$. Prepared by heating tetramethyldiaminodiphenylmethane with aniline and sulphur at 200° (G.P. 53614; Friedländer, 2, 60) ; or by heating Michler's ketone with aniline to 280° (Graebe, Ber. 1902, **35**, 2619) ; or by phenylating auramine (hydrochloride) with aniline (Fehrmann, Ber. 1887, **20**, 2851). The free base melts at 171° ; the salts are yellow to orange.

A large number of substituted phenyl auramines have been prepared by similar methods. Substitution in the *N*-phenyl group tends to deepen the shade of the dyestuff. Thus auramine itself gives pure yellow shades and *N*-phenyl- and *N*-*p*-tolyl-auramines, orange shades, whilst the corresponding compounds obtained by the use of *o*-toluidine, *m*-phenylenediamine, and the naphthylamines yield golden yellow, orange brown, and brownish-yellow shades respectively (G.P. 29060 ; Fehrmann, Ber. 1887, **20**, 2582).

Auramine G.—In this substance the substitution in the diphenyl methane part of the molecule is altered. *sym*-Dimethyldiamino-di-*o*-tolyl methane (from methyl *o*-toluidine and formaldehyde) is heated with sulphur, ammonium chloride and salt in dry ammonia at 175° (G.P. 67478; Gnehm and Wright, Ber. 1902, **35**, 913).



(III)

The commercial dyestuff is the hydrochloride (III). It has dyeing properties similar to Auramine itself but yields greener shades of yellow. The free base, $C_{17}H_{21}N_3$ (4 : 4′-*bis*-methylamino-3 : 3′-dimethylbenzophenoneimine) melts at 120°. The leuco base, obtained by reduction with zinc and acid, melts at 208°.

R. P. L.

AURANTIA. The ammonium salt of hexanitrodiphenylamine, formerly used as a dye.

AURINE and ROSOLIC ACID *v.* TRIPHENYLMETHANE DYESTUFFS.

AURIPIGMENTUM *v.* ARSENIC, ARSENIC TRISULPHIDE.

AUROBIN. Gold sodium thiosulphate (also termed sodium aurothiosulphate),

$$Na_3Au(S_2O_3)_2 2H_2O$$

Suggested for the treatment of tubercle and leprosy.

AUROCANTAN. Cantharidylethylenediamine aurocyanide.

AUROCHIN. *p*-Aminobenzoylquinine.

AUROPHOSPHINE *v.* ACRIDINE DYESTUFFS.

AUROSMIRID, found with iridosmine as small silver-white grains in the residues of Uralian platinum, insoluble in aqua regia. Analysis gave Ir 51·7%, Os 25·5%, Ru 3·5%, Au 19·3%, Fe trace. X-ray examination shows a face-centred cubic structure with *a* 3·816 Å (similar to that of iridium, for which *a* is 3·822 Å). The mineral is a solid solution of gold and osmium in cubic iridium ; whereas iridosmine is a solid solution of iridium, etc., in hexagonal osmium (O. E. Zvyagintzev, Compt. rend. Acad. Sci. U.R.S.S. 1934, 4, 176). L. J. S.

AURUM MUSIVUM or MOSAICUM. Mosaic gold. Made by triturating an amalgam of 2 parts tin and 1 of mercury with 1 part salammoniac and 1 of sulphur, and subsequently subliming. Used as a bronzing powder for plaster figures.

AUSTENITE. A solid solution of carbon in iron, as it exists above the transformation range or as preserved, with but moderate transformation, at lower temperatures, *e.g.* by rapid cooling or by the presence of retarding elements, as in 12% manganese steel or 25% nickel steel. In hardened high-carbon steel austenite forms a ground mass pierced by zigzag needles and lances of martensite; when the sole constituent, as in the above-mentioned manganese and nickel steels, it occurs as polyhedra, often coarse, and readily develops slip bands.

AUSTENITE. The chief constituent of turpentine-oils prepared from the turpentine of *Pinus australis.*

AUSTINITE. Hydrated arsenate of zinc and calcium, $2CaO\cdot 2ZnO\cdot As_2O_5\cdot 2H_2O$, as small colourless orthorhombic crystals which are bisphenoidal and right- and left-handed. Occurs with adamite at Gold Hill, Utah (L. W. Staples, Amer. Min. 1935, **20**, 112), and in Bolivia (F. Ahlfeld and R. Mosebach, Zentr. Min. A, 1936, 287). L. J. S.

AUSTRIAN CINNABAR. *Derby Red, Chinese Red.* Basic lead chromate,

$$PbCrO_4\cdot Pb(OH)_2,$$

an orange-scarlet pigment. Genuine cinnabar, mercuric sulphide, HgS, is mined at Idria, formerly Austrian, now part of Jugoslavia.

AUSTROCAMPHENE *v.* CAMPHENE.

AUTAN. A mixture of paraformaldehyde and the dioxide of barium or strontium, used in the disinfection of living rooms. On mixing the powder with water a rapid disengagement of formaldehyde vapour, mixed with oxygen, occurs.

AUTOCLAVES. Closed vessels capable of withstanding, at elevated temperatures, pressures greater than that of the atmosphere have long been used to facilitate chemical reactions. A well-known apparatus, the digester, introduced in 1681 by Dionysius Papin, a Huguenot refugee, who worked for a time with the Hon. Robert Boyle, is still employed in extracting nutritive matter from bones and other animal materials with the aid of superheated water. Such digesters are constructed of bronze or steel with bridge clamps and tightening screws of wrought iron. The safety valve working on the weighted lever principle was added by Papin, who is generally regarded as the inventor of this important fitting.

Included in the category of autoclaves are the sealed glass tubes and vessels which play a notable part in small-scale organic preparations. Occasionally the glass tube is reinforced by insertion into a closely fitting cold-drawn steel tube and in this case the glass tube is not sealed but is closed by a leaden washer fitted inside the screw cup of the steel tube.

For his researches on zinc dialkyls and other organo-metallic compounds Sir Edward Frankland, assisted by Nasmyth, the well-known inventor of the steam hammer, devised an autoclave of which the body and end-plate were forged from Low Moor iron. This cover was fitted with a cast-iron thermometer pocket and a weighted lever safety valve. The reagents were

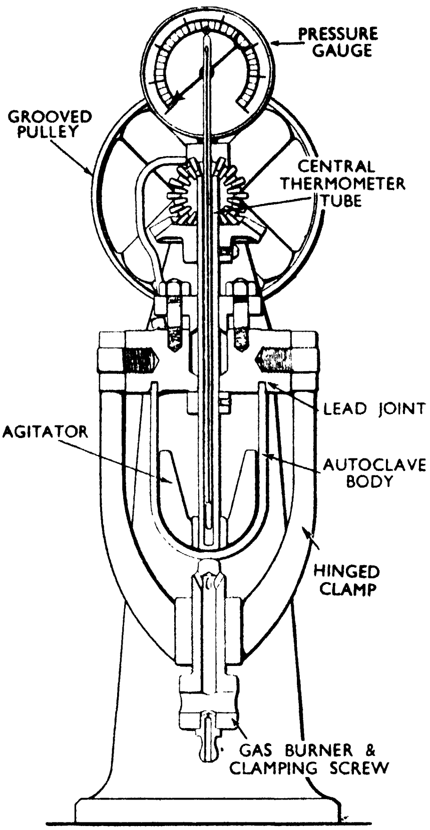


FIG. 1.—Autoclave with Horseshoe Clamp.

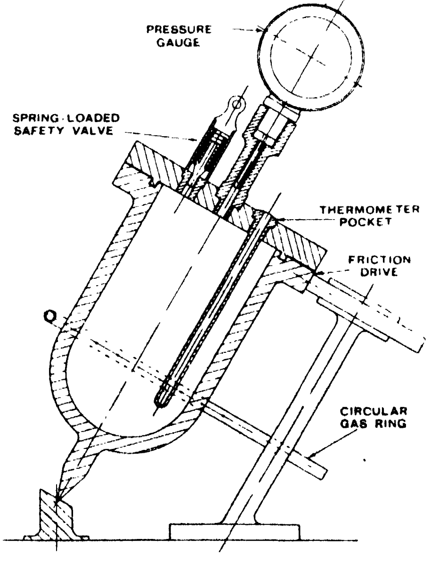


FIG. 2.—Rotating Autoclave.

enclosed in sealed glass vessels placed within the metal autoclave, which also contained some water or other liquid of suitable vapour pressure so that when the autoclave was heated there was equalisation of pressure between the inside and outside of the glass container.

The artificial colour industry has been a direct cause of development in the technique of autoclaves, because pressure is an essential factor in the preparation of many coal-tar intermediates required in dyestuff manufacture. These requirements necessitated improvements both in small- and large-scale pressure vessels.

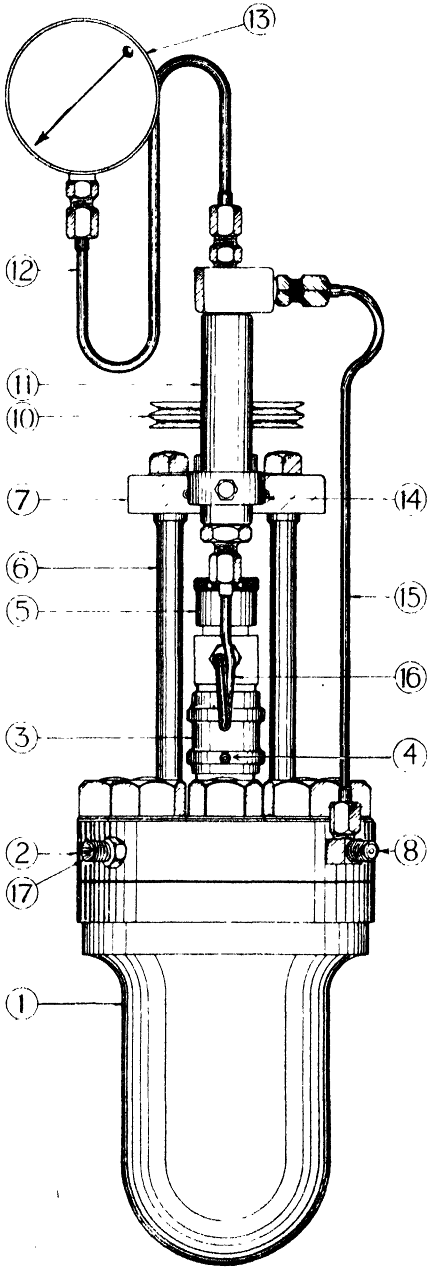


Fig. 3.—Scale Drawing of Autoclave.

Part No.	Name of Part.	Material.
1	Autoclave body	High tensile steel
2	Autoclave end plate	High tensile steel
3	Water jacket	Mild steel
4	Water cooling nipples	Mild steel
5	Gland nut	Mild steel
6	Crosshead supports	Mild steel
7	Crosshead, and thrust housing	Mild steel
8	Outlet connection for gas	High tensile steel
10	Driving pulley	Mild steel
11	Oil bottle	High tensile steel
12	Oil bottle connection to gauge	Nickel steel tube
13	Pressure gauge	Steel tube
14	Oil bottle clamp	Mild steel
15	Balance pressure pipe	Nickel steel tube
16	Oil bottle connection to gland	Nickel steel tube
17	Inlet connection for gas	High tensile steel

1. Laboratory Autoclaves.—Pre-war laboratory autoclaves were constructed in bronze or steel with lids screwed down by horseshoe clamps and carrying weighted lever safety valves working on the cup and cone principle. This type of autoclave did not admit of a stirrer, but more recently an ingenious modification has been introduced in which the horseshoe clamp is inverted (Fig. 1) so that stirring gear may be applied to the vessel, which is designed for a working pressure of 50 atmospheres.

Since 1916 rotating autoclaves have been employed in many laboratory experiments, and during the war these vessels were manufactured from high-explosive shell, the steel case of which was bored out until the thickness was about 2 cm. Such autoclaves (Fig. 2) have capacities ranging from 500 c.c. to 9 litres; they are available for temperatures up to 300° and for pressures up to 100 atmospheres.

The end-plate of this type of autoclave is fitted with pressure gauge, spring-loaded safety valve, and thermometer pocket. This last fitting assists in stirring the contents when the vessel is rotated by belt-driven friction gear. Heating is conveniently effected by a gas ring burner.

In many modern laboratory autoclaves the safety valve is omitted and during operation under pressure these vessels are surrounded with steel screens and explosion mantlets. All controls are effected outside these protective shields so that operators are protected in the event of accident. Effective agitation of the autoclave contents without loss of reagents or contamination by lubricants is a problem which has been solved by the use of stirring devices illustrated in Figs. 3 and 4. The former illustration is a scale drawing which shows in vertical section the body and end-plate of a 3-litre working capacity autoclave. The gland housing is water cooled and the steel stirrer shaft operates through a bronze lantern bush stirrer flanked on either side by leather and white metal washers. Lubrication of the shaft gland and washers is effected by a slight seepage of oil from a container maintained under the same pressure as the interior of the autoclave. When running under pressure, the upward thrust on the stirrer is taken by a housing which contains a heavy ball thrust bearing. This thrust housing is supported by stout steel pillars carried by the end-plate.

Particulars of the gland packing and oil lubrication are shown in Fig. 4.

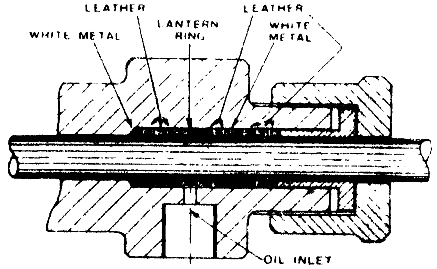


Fig. 4.—Details of Gland Packing.

The body and end-plate of such autoclaves, which range in capacity from 50 c.c. to 10 litres, are constructed from forgings of alloy steels specially selected because of their permanence and stability at high temperatures, which should not, however, exceed 500°.

The joint between the autoclave body and end-plate is of the single-sided spigot and recess pattern and is made with a soft copper gasket inserted between the joint faces, which are V-grooved to facilitate tightening. High-pressure valves are fitted to the end-plate for the introduction of fluids under pressure. For registering internal pressures, gauges of Bourdon type are employed with tubes constructed preferably in steel. This type of autoclave and its various accessories are shown in Fig. 5. Heating is external and may conveniently be effected with gas. As constructed in 18/8 nickel-chrome steel this apparatus may be operated up to 500° and under pressures up to 250 atmospheres.

Liquid materials under treatment are placed in open containers fitting closely into the interior of the autoclave. For many purposes "staybrite" steel containers are serviceable, but these are sometimes replaced by glass, silver or enamelled cast-iron containers. Owing to the high temperatures now attained lead is now no longer used either for containers or gaskets. The autoclave specified in the foregoing illustrations (Figs. 3, 4, and 5) is serviceable in a wide variety of chemical operations, of which the following are a few representative examples.

Hydrogenation.—The catalytic reduction process employed by Bennett and Noyes (1930) has been utilised in many directions in a 10-litre autoclave. Hydrogen under pressure is introduced into an alcoholic solution or suspension of a nitro-compound in presence of 1 % of platinic oxide (or alternatively of the same amount of palladium gel). At moderate temperatures (25° to 45°) and under pressures ranging from 2 to 40 atmospheres, reduction takes place smoothly, and after filtering or decanting from platinum metal the alcoholic solution contains no product other than the required amine. For instance, 2-nitrofluorenone is reducible at will to any one of the three stages, 2-aminofluorenone, 2-aminofluorenol, and 2-aminofluorene. This reduction process is especially useful in the preparation of unstable polyamines, which are readily destroyed by hydrolysis or aerial oxidation.

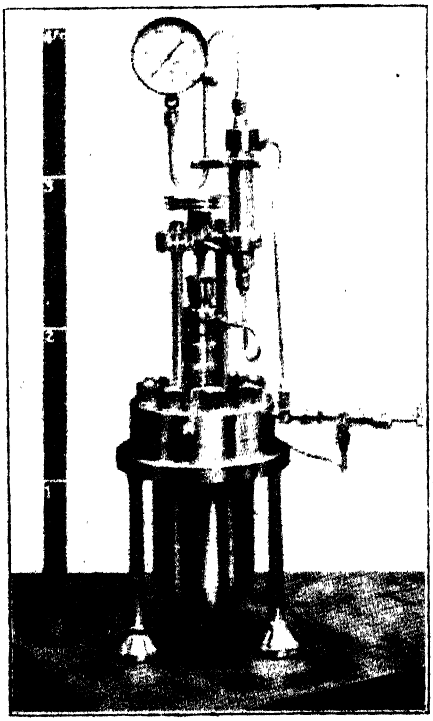


Fig. 5.—Autoclave of Nickel-Chrome Steel.

The resinoid constituents of low-temperature tar are hydrogenated to volatile oils when heated to 350° or 400° under 120 to 200 atmospheres of hydrogen in presence of molybdenum sulphide catalyst.

Dehydrogenation.—The converse process is conveniently effected when pyridine is heated with anhydrous ferric chloride at 320° and under 50 atmospheres pressure. The main product is 2 : 2′-dipyridyl, but there is also a useful by-product, 2 : 2′ : 2″-tripyridyl.

Carboxylations.—The Kolbe-Schmitt reaction and its modern variants are conveniently effected in such autoclaves. In presence of aluminium chloride, benzene and carbon dioxide at 100° and under 100 atmospheres combine to form benzoic acid and benzophenone. Other benzenoid hydrocarbons behave similarly and analogous carboxylations may be practised on phenols and aromatic amines.

Aminations.—When heated under pressure with ammonium chloride, ethyl alcohol furnishes a mixture of mono-, di-, and tri-ethylamines. The temperature required for this reaction is 320° and in stainless steel containers the pressure attained is approximately 100 atmospheres, largely due to the attack of ammonium chloride on the steel, which soon becomes perforated. With a silver container the pressure attained is only 60 atmospheres. This amination may be extended to phenols and is specially valuable with *m*-cresol and with *m*-5-xylenol, which give rise respectively to *m*-toluidine and *m*-5-xylidine, two bases not readily obtained from their parent hydrocarbons by successive nitration and reduction.

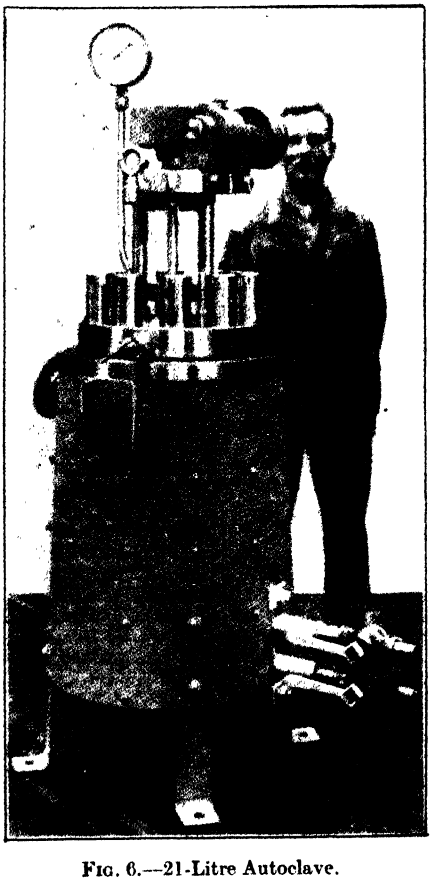


FIG. 6.—21-Litre Autoclave.

Condensations.—The Guerbet reaction (Compt. rend. 1901, **182**, 207) is a process which requires autoclave conditions, as it involves heating to 240° approximately of an alcohol and its sodium derivative. In this way *n*-propyl alcohol yields 2-methylpentanol and *n*-butyl alcohol gives 2-ethylhexanol.

Certain of the foregoing processes have passed into industrial practice after preliminary experiments on a semi-works scale. Fig. 6 represents a suitable autoclave for such intermediate trials. It is constructed of chrome nickel steel (**Cr** 18%, **Ni** 8%) and is heated externally. Its capacity is 21 litres and the operating conditions may be carried to 66 atmospheres at 350°.

II. Works Autoclave.—Large autoclaves suitable for works operations are now available from British sources. These vessels are manufactured for a wide variety of purposes and the materials of construction are adapted to the requirements of any particular chemical reaction. Acid-resisting autoclaves are manufactured in highly siliceous iron of tantiron type. For other requirements they may be made in cast iron, in cast or forged steel, in stainless steel, and in special nickel-chromium steels.

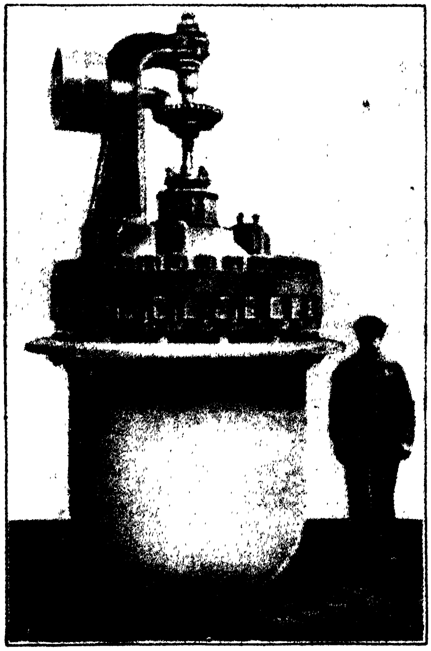


FIG. 7.—Works Autoclave in Cast Steel.

Fig. 7 shows a typical works autoclave in cast steel having the following proportion of elements other than iron: **C** 0·18, **Si** 0·15, **S** 0·05, **P** 0·05, **Mn** 1·25. This vessel is representative of the plant supplied to dyestuff manufacturers. It is used in aminations, as, for example, in the manufacture of β-aminoanthraquinone and of β-naphthylamine and its sulphonic acids. Such operations are on occasion continued for 48 hours at 180° to 210° under pressures approximating to 40 atmospheres. This autoclave is heated externally and various methods of firing may be employed. Several of these vessels may be mounted in series and the whole battery heated by coal fires or with producer gas. When the temperatures involved are not excessive, steam heating may be utilised.

Fig. 8 shows a vertical stainless steel steam-jacketed autoclave fitted with paddle agitator and fixed baffle plates.

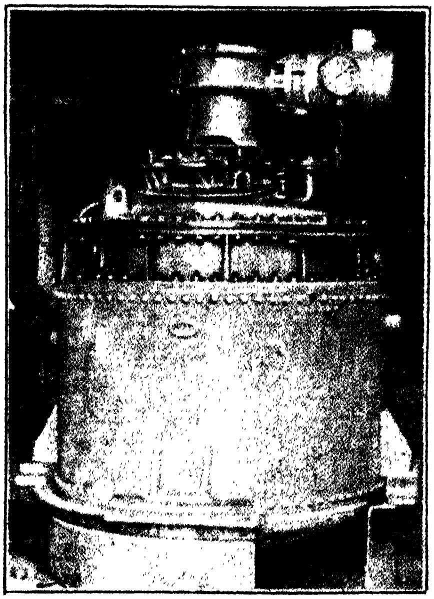


FIG. 8.—Steam-jacketed Autoclave.

The inner vessel and cover are constructed of welded staybrite steel, the cover being made in one piece. The diameter and depth of the inner vessel are both 3 ft. 6 in. The mild steel steam jacket is arranged to take up the difference in expansion between the two steels used. The working pressure in the inner vessel is 3 atmospheres and the steam pressure in the jacket is 4 atmospheres. The drive is by means of totally enclosed oil bath reduction gear with directly coupled electric motor. This plant is of general application for chemical operations at moderate temperatures and pressures.

Another type of works autoclave shown in Fig. 9 is a horizontal mild steel jacketed autoclave with heavy paddle agitators. The inner cylindrical vessel is 7 ft. long with 1 ft. 8 in. diameter ; it is made of solid drawn steel tube suitable for an internal working pressure of 66 atmospheres. The working pressure on the steam jacket would be 5½ atmospheres. The drive is arranged for fast and loose pulley belt drive, the power being transmitted through an enclosed oil bath worm gear. This autoclave is largely employed in the manufacture of fine chemicals. The steels employed in the construction of works autoclaves vary with the special requirements. For high internal pressures low alloyed steels are suitable ; these have a wide range of mechanical properties when appropriately heat treated. The chemical composition of such steels is indicated by the following typical analysis : C 0·3, Si 0·2, P and S 0·03, Mn 0·6, Cr 0·6, Mo 0·6, Ni 2·5, and the remainder Fe.

For operations in which resistance to corrosive fluids is the main desideratum the 18/8 chrome nickel steels may be used, a typical analysis of such an alloy being C 0·12, Si 0·3, P and S 0·03, Mn 0·8, Ni 8·0, Cr 18·0, and the remainder Fe. Small additions of other metallic elements may be made to suit particular requirements.

III. Superpressure Plant.—In the autoclaves described above, the working conditions do not exceed and in practice seldom attain pressures of 250 atmospheres and temperatures of 425°. At higher temperatures even heat-resisting steels tend to lose their resistance to deformation.

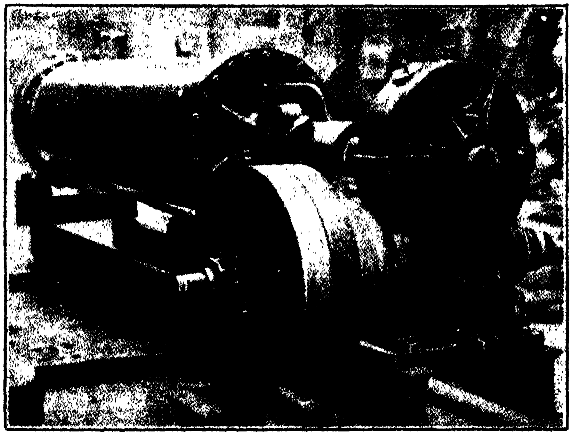


FIG. 9.—Horizontal Jacketed Autoclave.

For a special study of reactions under pressures of 3,000 atmospheres a special superpressure plant has been designed as illustrated in Fig. 10. The outfit consists essentially of a screw compression pump and an autoclave, the latter being shown without the oil bath which normally surrounds it during any operation requiring increased temperatures. Gases are introduced into the plant under 600–1,000 atmospheres pressure and compressed up to 3,000 atmospheres by means of the pump. The cylindrical autoclave is about 20 in. long with a ½-in. bore, giving a capacity of 110 c.c. The outside diameter is 11 in. The forgings for all the pressure-resisting parts of this plant are of heat-treated nickel-chrome-molybdenum steel having the following composition : **C** 0·29, **Si** 0·13, **S** 0·016, **P** 0·030, **Mn** 0·57, **Cr** 0·64, **Ni** 2·40, **Mo** 0·51 (remainder **Fe**). The pressure in this plant is measured by Bourdon gauges specially made to withstand the severe pressure conditions. When in operation the plant is sandbagged and wholly enclosed within a steel screen. The various controls are operated outside these protective shields.

G. T. M.

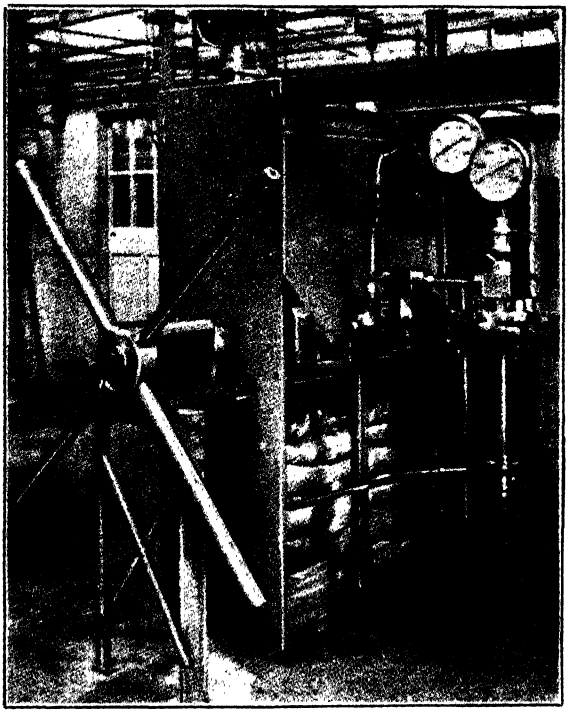


FIG. 10.—Superpressure Plant.

High Pressures and Liquid Phase Reactions.—In vessels subjected to internal pressures of the order of 5,000 atmospheres and upwards the inner layers of the walls are subjected to high-tensile hoop stresses comparable with the ultimate tensile strength of the steel, and there is a steep stress gradient in a radial direction through the walls. To increase the factor of safety in such vessels they may be built by shrinking two or more cylinders one over the other or by the auto-frettage process, the result in either case being to place the inner layers of the walls in an initial state of compression and the outer layers in tension. When the internal working pressure is applied there will be a much more even stress distribution in the walls than can be obtained with a mono-bloc cylinder of corresponding dimensions.

Apparatus for Developing a Working Pressure of 15,000 *Atmospheres.* — Fig. 1 shows in section an apparatus designed for carrying out liquid phase reactions at 15,000 atmospheres pressure. It is essentially a hydraulic ram, C being the high-pressure cylinder joined by the sleeve E to A, the low-pressure cylinder. C is built by shrinking together three cylinders, the two inner ones being made of high-speed steel, air-hardened at 1,250°C. and tempered at 600°C. ; their dimensions are such that the hoop stress due to shrinkage at the inner surface is 83·6 tons per sq. in. The low-pressure cylinder A, which may have to withstand an internal pressure of 2,000 atmospheres, is made by shrinking together two cylinders, and has an internal diameter of 2·5 in. The two pistons B and D are made of " race " steel and are ground and lapped into their respective cylinder ; the low-pressure piston is obturated by a Bridgman packing, K (" Physics of High Pressure," G. Bell and Sons, Ltd., 1931, p. 39), and the high-pressure piston by a Poulter packing, J (Phys. Rev. 1932, **40**, 860).

The apparatus is mounted vertically and the reactants are enclosed in a glass vessel over mercury, placed in the upper cylinder; the remaining space is filled with a suitable liquid for transmitting the pressure. By means of a hand pump an initial pressure of 1,000 atmospheres is applied through the side opening G. Pressure is then transferred to the cylinder A and is transmitted and "stepped-up" by the advance of the piston D into the upper cylinder.

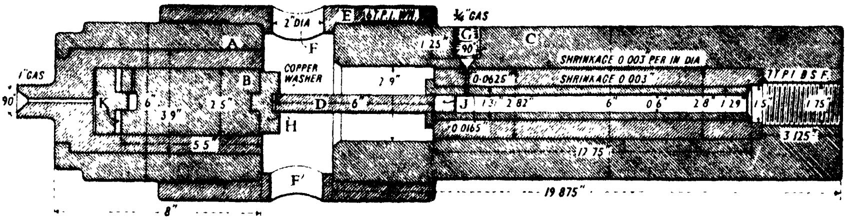


FIG. 1.

The effect of very high initial pressures upon liquid phase reactions is in general (*a*) to increase the velocity of attainment of equilibrium, (*b*) to increase the equilibrium proportions of the product or products formed with a diminution in volume according to the Le Chatelier principle, (*c*) to induce liquid phase reactions which do not occur to a detectable extent at atmospheric pressure, and (*d*) in some instances to alter the course of the reaction.

Examples illustrating all these effects are known; thus it has been found that *cyclo*-pentanone and cyanacetic ester react in the presence of M/20 piperidine to give *cyclo*-pentylidene cyanacetic ester, the pressure effect being as follows:

Pressure (atms.).	*Cyclo*pentylidene cyanacetic ester (per cent.).
1	3
500	50
15,000	100

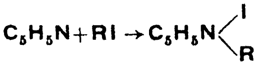
Also, whereas at atmospheric pressure and 60° no reaction takes place in the absence of a catalyst, at 5,000 atmospheres a 26% condensation occurs. Condensations of this type are generally inhibited at atmospheric pressure by α-substituents, but take place readily when the pressure is increased to about 3,000 atmospheres.

The velocity of attainment of equilibrium in esterifications and hydrolyses is usually influenced to a marked degree by increase of pressure. Thus in the system:

$$\mathrm{CH_3{\cdot}COOH + C_2H_5{\cdot}OH \rightleftharpoons CH_3{\cdot}COO{\cdot}C_2H_5 + H_2O}$$

the effect of raising the pressure from 1 to 5,000 atmospheres is to increase the velocity constant nearly 30-fold.

A similar change in the constant is found in reactions of the type:



$$\mathrm{C_5H_5N + RI \rightarrow C_5H_5N{<}^{I}_{R}}$$

In acetone solution at 40°C. the reaction between pyridine and ethyl iodide, for example, is increased 7·2 times at 2975 kg./cm.^{2} and 47·5 times at 8,500 kg./cm.^{2} (Proc. Roy. Soc. 1935, A, **150**, 223). D. M. N.

AUTOLYSIS.—Salkowski (1889) described the phenomenon of autolysis as one of self-digestion of tissue proteins and showed its similarity to the process of digestion in the alimentary tract. Auto-digestion of liver, spleen and other tissues was found to give rise to leucine and tyrosine. A marked advance in the study of autolysis was made by Jacoby (Z. physiol. Chem. 1900, **30**, 149, 174; 1901, **33**, 126), who, considering the problem from the point of view of the pathologist, found (*a*) that autolysis of liver gives rise to the end products of protein hydrolysis, and (*b*) that liver poisoned by phosphorus digests more rapidly and completely than the normal tissue, and can liberate into the blood, even of the living animal, enzymes which digest fibrinogen and therefore interfere with the process of clotting. He showed that liver residue, after prolonged autolysis of the organ, consists of nucleins, connective tissue debris and a soluble albumin, the globulin fraction having been digested. If a lobe of liver be tied off for several hours in the surviving animal, amino acids accumulate.

The process of autolysis, and the enzymes which are actively engaged therein, are not simply post-mortem phenomena; they occur in the living organ and are there linked up with, and influenced by, other processes so that the dynamic equilibria characteristic of living tissues obtain.

Jacobi found some specificity of attack by the enzymes of autolysing liver, for they would not apparently digest lung tissue.

A common practice in autolytic studies is to add an antiseptic, such as toluene, to the tissue to prevent bacterial digestion; it is possible that such studies are open to criticism on the grounds that the antiseptic itself may influence the activities of the autolytic enzymes, however toluene is probably one of the safest antiseptics for use in autolytic work.

The results of early work on autolysis have been summarised by Bradley (Physiol. Rev. 1922, **2**, 415). Briefly, they are as follows: (*a*) all the tissues examined will autolyse to a greater or lesser extent, the epithelial tissues being hydrolysed most rapidly and completely;

(*b*) certain tissues, *e.g.* liver, kidney, and thymus, autolyse more rapidly in the presence of salts of such metals as Mn, Co, Fe, Pt, and in the presence of weak acids; (*c*) the rate of autolysis is retarded by alkaline conditions; (*d*) foreign matter, added to the tissue, may also be hydrolysed.

Dernby (Biochem. Z. 1917, **81**, 107 ; J. Biol. Chem. 1918, **35**, 179) has advanced the views that enzymes engaged in autolysis are mixtures of pepsin, erepsin and trypsin, his evidence being derived from studies of protein digestion by autolytic enzymes at various hydrogen ion concentrations. Rona also believes that in liver autolysis a true peptic activity takes place. Bradley (*ibid.* 1922, **52**, 467) contends, however, that trypsin or pepsin, as recognised in pancreatic trypsin or gastric pepsin, do not exist as such among the autolytic enzymes. There is evidence of an enzyme complex, a "primary protease," which digests acid salts of the tissue proteins between $p_{\rm H}$ 7 and 3, this process being completely inhibited at $p_{\rm H}$ 2·6 (whereas pepsin is active at $p_{\rm H}$ 1), and there is also evidence of an ereptic type of enzyme which digests the primary cleavage products of proteins to amino acids, this enzyme being active between $p_{\rm H}$ 8 and 3. Hertzmann and Bradley (J. Biol. Chem. 1924, **62**, 231 ; 1925, **63**, 37) present the following picture of the initial steps of autolysis: "The first step in the process is believed to be the combination between the primary protease and the native proteins of the tissue cells. During life and at the normal $p_{\rm H}$ of the cell the protease probably exists in this combined form. At the $p_{\rm H}$ of 7·4 most of the tissue proteins are in the form of their base salts. This form is stable and no cleavage results. When, however, acid develops in the mixture acid proteins are formed, unstable in combination with the enzyme and with a weakened peptide bond. Under these conditions, cleavage follows." These primary cleavage products are further hydrolysed by cell erepsin. The addition of foreign proteins may inhibit autolysis by forming a stable combination with a part of the protease.

The two important factors leading to a development of autolysis are (*a*) deprivation of oxygen to the tissue, (*b*) an increase of hydrogen ion concentration in the tissue. The optimum $p_{\rm H}$ for autolysis is between 6·6 and 6·8, such a $p_{\rm H}$ being developed in tissues during asphyxiation.

The end products of autolysis closely resemble those from tryptic digestion, but substances other than proteins are also broken down, *e.g.* glycogen, fats and nucleoproteins, with the production of lactic acid, fatty acids and purines. Ammonia is commonly produced.

Not only mammalian tissues, but yeast cells and bacterial cells will undergo autolysis; in fact, autolytic methods are often used as a means of obtaining cell-free enzymes from micro-organisms, *e.g.* lactic acid dehydrogenase from *B. coli* and yeast, invertase from yeast and moulds.

It is probable that once a living cell is placed in an environment where, either through deprivation of metabolites or of oxygen, energy-producing processes leading to cell syntheses can no longer be accomplished at their normal rates, autolytic processes appear and gradually become dominant. Some of the known biochemical consequences of deprivation of oxygen to a living tissue may be noted:—

(*a*) Glycolysis (lactic acid production from glucose or glycogen) is usually greatly inhibited by the presence of oxygen. This phenomenon, termed by Warburg the "Pasteur Effect," is characteristic of normal living tissues. Oxygen deprivation leads to a great increase in lactic acid formation and hence of the hydrogen ion concentration in the tissue.

(*b*) Organic esters of phosphoric acid are present in living tissue and depend ultimately for their existence in normal proportions on energy-yielding reactions. Deprivation of oxygen leads to an alteration of equilibria with resultant formation of free phosphoric acid.

(*c*) The syntheses of urea and glutamine in intact tissue depend on energy-yielding reactions. Deprivation of oxygen leads to an alteration of ammonia metabolism. Glutamine is broken down by a specific enzyme to glutamic acid and ammonia, and the latter cannot be built up into urea. Sometimes, *e.g.* with retina, the presence of glucose, even in absence of oxygen, will allow glutamine synthesis to occur—but presumably the synthesis depends on the energy yielded by the anaerobic breakdown of glucose (Krebs, Biochem. J. 1935, **29**, 1951). It is likely that the enzyme responsible for the hydrolysis of glutamine is also responsible for its synthesis and this may be an example of a general rule.

(*d*) It is known that thiol compounds exist in the living cell and that a dynamic equilibrium is set up between thiol compounds, disulphide compounds, and oxygen (Hopkins and Elliott, Proc. Roy. Soc., *B.* 1931, **109**, 58). Absence of oxygen will tend to bring about an increase in concentration of thiol compounds which, it is known, increase the activities of such hydrolytic enzymes as papain and cathepsin (Purr, Biochem. J. 1935, **29**, 5, 13).

It is obvious that deprivation of oxygen tends to produce conditions favourable for the commencement of autolytic breakdown of tissue cells. As soon as the cell structure is modified or when it disintegrates, numerous other metabolic processes, normal to the living cell, are affected. For example, the power of liver tissue to oxidise fatty acids is practically eliminated by simply mincing the tissue (Quastel and Wheatley, Biochem. J. 1933, **27**, 1753) ; bacteria which have undergone lysis lose most of their dehydrogenase activities (Penrose and Quastel, Proc. Roy. Soc., *B.* 1930, **107**, 168) ; crushed liver can no longer synthesise urea from free ammonia (Krebs and Henseleit, Z. physiol. Chem. 1932, **210**, 33) ; blood cells after lysis can no longer hydrolyse methylglyoxal owing to the escape of a necessary co-enzyme—glutathione—from the cells (Jowett and Quastel, Biochem. J. 1933, **27**, 486).

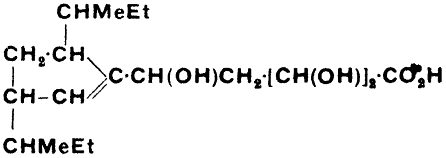
Thus, autolysis may be regarded as due to a series of reactions set up as a result of the initial disturbance of the metabolic equilibria. The reactions are due to catalysts, previously inert or stabilised, being brought into activity by the altered environmental conditions, and to catalysts being brought into contact with substrates previously held remote from them by the conditions obtaining in the living cell. Altered cell equilibria and destruction of normal cell enzymes and products induce the "biochemical chaos" which marks the dissolution of the cell. (Further literature on the subject of autolysis will be found on reference to "Die Fermente und Ihre Wirkungen," Oppenheimer, G. Thieme, 1925. The subject is also treated exhaustively by Haehn, Ergeb. d. Enzymforschung, 1936, **5**, 117). J. H. Q.

AUTUNITE or CALCO-URANITE. A mineral consisting of hydrated phosphate of uranium and calcium, $Ca(UO_2)_2P_2O_8,8H_2O$, which within recent years has been somewhat extensively mined as an ore of uranium and radium (UO_3 55–62%). It is a member of the isomorphous group of minerals known as the "uranium micas," which crystallise as square, tetragonal (or very nearly square, orthorhombic) plates with a perfect micaceous and pearly cleavage parallel to their surface. In the orthorhombic autunite the colour is characteristically sulphur-yellow, or sometimes with a greenish tinge, so that this mineral is readily distinguished from the emerald-green torbernite or cupro-uranite. Sp.gr. 3·1; H. 2–2½. It occurs as an alteration product of pitchblende, and is often found as a scaly encrustation on the joint-planes of weathered granite or gneiss. The more important localities are St. Symphorien, near Autun in France (hence the name autunite); St. Just, Redruth, and Grampound Road in Cornwall; Johanngeorgenstadt and Falkenstein in Saxony; Black Hills in South Dakota; Olary and Mount Painter in South Australia; Madagascar; and Sabugal near Guarda in Portugal. At the last-named locality several mines have recently been opened up; the crude ore is here leached with sulphuric acid, and the extracts sent to Paris for further treatment. L. J. S.

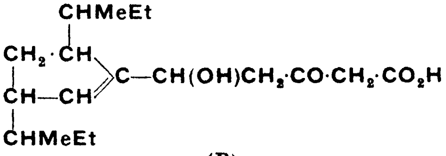
AUXIN (including hetero-auxin). A plant hormone or growth-regulating substance. Occurs generally in the plant kingdom (notably in actively growing apical tissue and in pollen), in certain fungi and yeasts, in urine and in various animal organs. It exerts a controlling influence on the vegetative development of plants, tending generally to promote apical growth of stems and shoots and to restrict the growth of roots. Earlier work of Went and others showed that auxin was closely associated with the stretching of plant cells, as a result of which it induces a curvature in decapitated coleoptiles[1] when applied asymmetrically to the cut stumps. This is the basis of Went's classical test of the potency of auxin preparations (one "*Avena* unit" is the amount of growth-substance to cause a deflection of 10°). The average activity of auxin-A is 5×10^{10} *Avena* units per g., *i.e.* 0·00002γ cause a 10° curvature. The translocation of auxin within the plant system under external stimuli is intimately associated with, if not the primary cause of, geotropism, phototropism, and electropism in plants. The action of auxin on the aerial parts of plants is to a large extent the reverse of that on roots.

In 1933 Kögl, Erleben, and Haagen-Smit (Z. physiol. Chem. 1933, **216**, 31) obtained about 0·39 g. of auxin from urine and showed it to be a monobasic acid of the formula $C_{18}H_{32}O_5$, m.p. 196°, lactone, m.p. 173°, $[\alpha]_D^{20}$ $-3{\cdot}19°$ and $-3{\cdot}44°$ respectively (in alcohol), both mutarotatory, containing three hydroxyl groups readily yielding an equally active lactone with which it is probably associated in nature.

In subsequent investigations of the constitution Kögl and colleagues (*l.c.* and *ibid.* 1933, **220**, 137, 162) found many samples of vegetable origin contained a second hormonal substance isomeric with auxin lactone and containing a keto- as well as a hydroxyl group. This was designated auxin-*B* $C_{18}H_{30}O_4$, m.p. 183°, in contradistinction to Went's original auxin-*A*. Both auxin-*A* and -*B* yielded on oxidation a dibasic acid $C_{13}H_{24}O_4$, subsequently identified by Kögl as *aa′*-di-*sec.*-butylglutaric acid. The two auxins therefore were represented as:



(A)



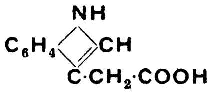
(B)

Auxin-*B* differs from auxin-*A* in being insoluble in ether and in its relatively greater resistance to heat and oxidation. It gives no reaction in Went's coleoptile test, but accelerates the regeneration of yeast cells and the production of mycelium of a number of fungi. Among the latter certain *Murcorineæ* synthesise auxin-*B* in purely synthetic media, whereas others, *e.g. Phycomyces*, do so only when supplied with vitamin-*B*. In some respects the physiological activity of auxin-*A* and auxin-*B* seems closely related to that of vitamin-B_1, and a constitutional relationship between these substances appears more than a possibility. According to Hartelius (Biochem. Z. 1933, **261**, 76, 89), the full activity of auxin-*B* is exerted only in the presence of a co-substance. Certain zinc salts seem to function in this respect.

In further investigations, Kögl and Kostermans (Z. physiol. Chem. 1934, **228**, 90, 104, 113) established the presence in urine of a third growth-promoting substance, which possessed certain of the physiological activities of the auxins, including a positive coleoptile reaction. Other workers have shown this substance to possess a marked tendency to induce root initiation on plant stems, to check the development of axial buds, and to cause epinasty[1] in leaves. It also stimulates the development of certain moulds in a manner similar to that of auxin-*B*. Kögl designated this substance "heteroauxin" and subsequently identified it as indole-3-acetic acid,

---

[1] The first emerging ensheathed leaf from the germinated seed.



Earlier conceptions of a specificity of physiological action of the auxins have more recently become much modified, and it now seems more probable that the specific action on plants is to be associated with a particular type of molecular structure rather than with individual substances. Thus Kögl has shown that hydrogenation or esterification of auxin-*A* results in complete loss of hormonal activity. On the other hand, although hydrogenation destroys the activity of heteroauxin a number of its esters and simple derivatives retain varying degrees of hormonal potency (Z. physiol. Chem. 1934, **28**, 90 ; 1935, **235**, 181, 201). For example, the following are active :

1-Methylindole-3-acetic acid (ethyl ester inactive).
2-Methylindole-3-acetic acid (methyl ester inactive).
5-Methylindole-3-acetic acid (methyl ester active).
Indole-3-pyruvic acid.
Indole-3-α-propionic acid.

On the other hand, the following are inactive :

Dihydroindole-3-acetic acid.
2-Ethylindole-3-acetic acid.
2:5-Dimethylindole-3-acetic acid.
l- and *r*-Indole-3-lactic acids.
Indole-2- and -3-carboxylic acids.
Indole-3-β-propionic acid.

Hitchcock (Contr. Boyce Thompson Inst. 1935, **7**, 87) has shown the activity of :

Indole-3-α-propionic acid.
β-Phenylacrylic acid.
β-Phenylpropionic acid.

Zimmerman and Wilcoxon (Contr. Boyce Thompson Inst. 1935, **7**, 209) have added to the list of plant hormones :

α- and β-Naphthylacetic acid.
Acenaphthyl-5-acetic acid.
Phenylacetic acid.
Fluorenylacetic acid.
Anthracylacetic acid.
Indolylbutyric acid.
α-Naphthylacetonitrile.

Manske and Leitch (Canad. J. Res. 1936, **14**, B, 1) record the activity of :

Indole-3-δ-valeric acid.
4-Methylindole-3-β-propionic acid.
Indole-1 :3-diacetic acid.

According to Thimann (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 896) indene-3-acetic and coumaryl-1-acetic acid are biologically active, although the latter does not give the coleoptile reaction and neither are readily translocated within the plant system. Other growth-substances examined by Haagen-Smit and F. W. Went (*ibid.* p. 852) exhibit growth-stimulating properties but differ from the auxins in causing neither curvature of coleoptiles nor bud inhibition, and in exhibiting no polar transport. *allo*-Cinnamic acid has a high cell-elongating power, whereas cinnamic acid is inactive.

These and similar investigations have led to the suggestion that the various so-called growth-regulating substances are not the *immediate* causal agents of the growth phenomena concerned, but that they operate by inducing in the plant cell the same fundamental change, which effects the visible modification of structural development.

Recent work at the Boyce Thompson Institute draws attention to the similarity between the action on plants of growth-substances and that of ethylene. Gaseous emanations from various plant tissues give reactions of ethylene and it is further shown that application of growth-substances to plants increase these emanations. The exact relationship between these substances is by no means clear, but the observations lend support to the theory that auxins and heteroauxin, in common with numerous other substances, serve as activators of a definite chemical change or series of changes resulting in controlled, stimulated or modified growth in plants. A. G. Po.

AVENTURINE or AVANTURINE. A variety of quartz spangled throughout with minute yellow scales of mica, found at Capa de Gata, Spain, is known as aventurine quartz. An aventurine felspar or sunstone is found at Tvedestrand, Norway, and is used for ornaments.

Artificial aventurine, or *glass*, or *gold flux*, was manufactured for a long period at the glass-works of Murano near Venice. It may be prepared by adding to 100 parts of a not too refractory glass, 8 to 10 parts of a mixture of equal parts of ferrous and cuprous oxides, and, after fusion, allowing the mixture to cool very slowly so as to facilitate the formation of crystals.

Aventurine glaze for porcelain, invented by Wöhler (Annalen, 1849, **70**, 57), is prepared by finely grinding 31 parts Halle kaolin, 43 quartz sand, 14 gypsum, and 12 porcelain fragments; making the whole into a paste with 300 parts water, and adding successively 19 parts potassium dichromate, 47 lead acetate, 100 ferrous sulphate, and sufficient ammonia to precipitate the whole of the iron. After the soluble potash and ammonium salts have been washed out, the glazing is ready for use.

AVERTIN. *Ethobrome*, βββ-tribromoethyl alcohol, $CBr_3{\cdot}CH_2{\cdot}OH$, a white crystalline powder, prisms, m.p. 80°, b.p. 92°–94°/11 mm. A solution of the alcohol in amylene hydrate is used as a basal hypnotic—premedication narcotic (*v.* ANÆSTHETICS).

AVIGNON GRAINS. The seeds of ***Rhamnus infectorius*** employed in dyeing for the production of yellow colours (*v.* PERSIAN BERRIES).

---

[1] The downward bending of leaves, leaf-stems, etc., due probably to more rapid growth of upper than of lower surfaces.

AVIGNON or FRENCH BERRIES. The dried fruits of *Rhamnus infectorius* and of *R. alaternus* are used for dyeing yellow or orange shades on mordanted wool.

AVIONAL *v.* ALLOYS, LIGHT.

AVOCADO OIL. This fatty oil is obtained from the edible, oleaginous fruit-pulp of the avocado-pear (*Persea gratissima*, Gaertn. *N.O.* Lauraceæ) which is a native of tropical America and cultivated extensively, particularly in California, as a table-fruit. Ripe but blemished fruits, which are unsuitable for table consumption, are worked up for the sake of the oil which is expressed in the cold from the stripped, dried fruit-flesh. Trinidad avocados yield rather less oil than the Californian fruit which may contain as much as 15–30%, *i.e.* about 50–70% of oil on the dried pulp. The oil is non-drying, having an iodine value of about 95 and a sp.gr. about 0·913 at 25°C.; the component fatty acids consist chiefly of oleic, linolic and palmitic acids (Jamieson, Baughman and Hann, Oil and Fat Ind. 1928, **5**, 202). The avocado pulp is stated to be rich in vitamin A and also to contain appreciable quantities of the fat-soluble vitamins E and D (*cf.* Weatherby, Yontz and Watson, J. Home Econ. 1929, **21**, 360 ; Weatherby, Calif. Avocado Assoc. Yearbook, 1930, 100 ; Exp. Sta. Rec. **64**, 587 ; Robbins and Bilger, Hawaii Agric. Expt. Stat. Rept. (1933), 1934, p. 23). The oil is highly valued as an ingredient of pharmaceutical and cosmetic preparations; although it would be quite suitable for the manufacture of soap, it is at present too expensive to be used for this purpose (*cf. also* W. Popenoe, " The Avocado in Guatemala," U.S. Dept. Agric. Bull. No. 743, 1919 ; Dept. Agric. Trinidad and Tobago, Bull. 1919, **18**, 113). E. L.

AVOCADO PEAR, *Alligator Pear.* The fruit of *Persea gratissima.* The fleshy, rind-covered fruit contains a large stone or " pit " weighing 1–1¼ oz., *i.e.* about a quarter of the weight of the fruit. Analyses recorded show considerable variations, partly attributable to differences of growth conditions and variety, but also to the fact that in most cases the fruit is gathered while still " firm " and allowed to soften during storage. It is during the period of late development and ripening that rapid changes in composition take place. There is some difference of opinion as to the required stage at which the fruit should be gathered. Stahl (Florida Agric. Exp. Sta. Bull. 1933, No. 259) has made an extensive examination of the fruit and records the following ranges of composition during the development and ripening stages: water 64–89%, ash 0·08–1·58%, protein 0·53–2·1%, oil 0·4–20·6%, total sugars 0·4–2·7%. Even in the period over which the fruit may be gathered variations in composition may be considerable, thus :

H_2O	Ether extract.	Protein.	Total sugar.	Reducing sugar.	Ash.
63–84	6·5–18·5	1·5–2·3	0·84–2·7	0·8–2·6	0·8–1·2

In the final stages of development there occurs a rapid increase in ether extract and, to a smaller extent, in protein and ash, and a decrease in water content and total sugars. During the storage of fruit picked in a firm condition, there is a further increase in oil and hydrolysable sugars and a decline in total and reducing sugars. The percentage of oil reaches a maximum at absolute maturity and Stahl suggests it may be regarded as an index of this stage. The ether-soluble matter includes about 4% of resins and an essential oil resembling that of bergamot, which has an iodine value of 29·9 and saponification value 207. In the ripe fruit, La Forge (J. Biol. Chem. 1916, **24** ; 1917, **28**, 511) identified a sugar, m.p. 152°, $[\alpha]_D^{20}+27{\cdot}17°$, probably a mannoketoheptose (*see also* F. E. Wright, *ibid.* 523). A. G. Po.

AVOGADRITE. Potassium fluoborate, KBF_4, containing up to 9·5% $CsBF_4$, occurring as minute orthorhombic crystals of the baryte type in a mixed saline encrustation on Vesuvian lava. Named after Amedeo Avogadro (1776–1856) (F. Zambonini, Atti R. Accad. Lincei, 1926 [vi], **3**, 644 ; G. Carobbi, *ibid.* 1926 [vi], **4**, 332). L. J. S.

AWOBANA. The blue colouring matter of the Japanese flower " Tsuyukusa " (*Commelina communis*), used in the preparation of awobana paper, has been isolated by Kuroda (Proc. Imp. Acad. Tokyo, 1931, **7**, 61 ; 1933, **9**, 94). The pure pigment, an anthocyanin, yields phloroglucinol and gallic acid when fused with alkali and is thus considered to be a monoglucoside of delphinidin.

A pale yellow co-pigment is also present and this, by decomposition with alkali, gives *p*-coumaric acid and *p*-hydroxyacetophenone. A. G. Po. and E. J. C.

AXIN. A secretion of a Mexican rhynchotrus insect *Llaveia axinus* which feeds on *Spondias lutea*, *Xanthoxylum clavaherculis*, and *X. pentanome*, is a yellow buttery fat, m.p. 38°, soluble in hot alcohol and ether. It absorbs oxygen rapidly, becoming dark brown, hard and insoluble, resembling Japan lac and forms an excellent lacquer for wood, metals, and pottery (Bocquillon, J. Pharm. Chim. 1910, **2**, 406 ; J.S.C.I. 1910, **29**, 1320).

AXINITE. A complex borosilicate of aluminium, calcium, iron and manganese. Various formulæ have been proposed : W. E. Ford (1903) gives $R''_7R'''_4B_2(SiO_4)_8$, where $R''=Ca$, Fe, Mn, Mg or H_2, and $R'''=Al$ or Fe. According to W. T. Schaller (1909) the composition is expressed as isomorphous mixtures of " ferro-axinite,"

$$4CaO{\cdot}2FeO{\cdot}2Al_2O_3{\cdot}B_2O_3{\cdot}8SiO_2{\cdot}H_2O,$$

and " manganaxinite,"

$$4CaO{\cdot}2MnO{\cdot}2Al_2O_3{\cdot}B_2O_3{\cdot}8SiO_2{\cdot}H_2O$$

The mineral contains 5–6% B_2O_3. Crystals are triclinic with a characteristic axe-shaped habit, hence the name. The colour is usually clove-brown, but may be yellowish or greenish. D 3·03–3·36, H 6½–7. Axinite occurs in crystalline schists and metamorphic rocks at many localities. Fine crystals, suitable for cutting as gem-stones, are not uncommon from Bourg d'Oisans, Isère, France, and large groups of crystals come from Japan. In the metamorphic rocks surrounding the granite mass of

Bodmin, in Cornwall, massive axinite and axinite-rock are of abundant occurrence (G. Barrow, Min. Mag. 1908, **15**, 113 ; “ Geology of Bodmin and St. Austell,” Mem. Geol. Survey, 1909).

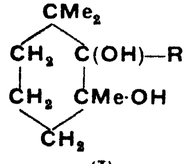
Tourmaline (*q.v.*), another complex borosilicate containing rather more boron (B_2O_3 9–11%), is also of common occurrence under the same conditions in Cornwall. L. J. S.

AZABENZANTHRONE *v.* ANTHRAQUINONE DYESTUFFS.

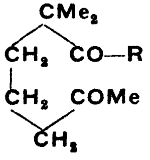
AZADIRACHTA INDICA or MELIA AZADIRACHTA (L.). *Indian Lilac Tree.* An infusion of the bark (neem or margosa bark) is used in India as a medicinal bitter. The fatty oil (margosa oil), from the seeds, examined by Lewkowitsch (Analyst, 1903, 432), had the following properties: d_{16}^{16} 0·9142 ; saponification value, 196·9 ; iodine value, 69·6.

AZAFRAN or AZAFRANILLO *v.* AZAFRIN.

AZAFRIN, $C_{27}H_{38}O_4$, the pigment of the azafranillo root, *Escobedia scabrifolia* (Fam. Scrophulariaceæ), forms deep orange prisms, m.p. 212°, from acetone-toluene. The pigment is lævorotatory ($[\alpha]_{Cd}^{20}$ $-75°$ in ethyl alcohol) and shows absorption maxima in carbon disulphide at 476, 445, and 419 $m\mu$. An ethereal solution of azafrin on shaking with hydrochloric acid gives a deep violet acid layer due to the formation of a hydrochloride; similar treatment with other acids gives rise to corresponding salts, *e.g.* sulphate and perchlorate. Kuhn, Winterstein, and Roth (Ber. 1931, **64** [B], 333) showed that complete hydrogenation involves the saturation of seven double bonds; they also found that azafrin was a monocarboxylic acid, forming a monomethyl ester, methylazafrin (orange leaflets, m.p. 193°, from methyl alcohol, $[\alpha]_{Cd}^{20}$ $-73°$ in ethyl alcohol) and also contains two hydroxyl groups which fail to acetylate and are therefore probably tertiary. Kuhn and Deutsch (Ber. 1933, **66** [B], 883) showed that perhydroazafrin reacts with one molecule of lead tetra-acetate, the resulting product, perhydroazafrinone, exhibiting no aldehydic properties. They further ascertained that regulated potassium permanganate oxidation of the pigment (*see* CAROTENOIDS) yields geronic acid, indicating that no secondary groupings can exist in the terminal ionone ring. Azafrin is therefore a di-tertiary glycol-monocarboxylic acid and these authors propose the formulation (I). In accordance with this, regulated chromic oxidation of azafrin yields azafrinone (II) (orange red plates, m.p. 191°, from acetone; monoxime, m.p. 194°), a diketo-monocarboxylic acid which is optically inactive, proving that the activity of the pigment itself must be due to the hydroxyl groups.



(I)



(II)

where $R=\cdot[CH:\dot{C}H{\cdot}CMe:CH]_2{\cdot}CH:CH{\cdot}CH:CMe{\cdot}CH:CH{\cdot}CO_2H$

I. M. H. and R. F. P.

AZANTHRAQUINONE *v.* ANTHRAQUINONE DYESTUFFS.

AZELAIC ACID, lepargylic acid, *n*-heptanedicarboxylic acid, $CO_2H[CH_2]_7{\cdot}CO_2H$.

Azelaic acid is found in rancid fat (Scala, Chem. Zentr. 1898 [i], 439) and may be obtained by oxidising Chinese wax, cocoanut oil or castor oil with nitric acid (Buckton, J.C.S. 1857, **10**, 303; Wirz, Annalen, 1857, **104**, 261 ; Arppe, *ibid.* 1862, **124**, 86) or by oxidising oleic acid or keratin with permanganate (Ehmed, J.C.S. 1898, **73**, 627; Lissizin, Z. physiol. Chem. 1909, **62**, 226). Synthetically it has been obtained from pentamethylene dibromide and ethyl sodiomalonate (Haworth and Perkin, J.C.S. 1894, **65**, 86), but it is most conveniently prepared by permanganate oxidation of ricinoleic acid obtained by hydrolysis of castor oil (Hill and McEwen, Organic Syntheses, 1933, **13**, 56 ; Verkade, Rec. trav. chim. 1927, **46**, 137); for the mechanism of this reaction, *see* Asahima and Takimoto (J. Pharm. Soc. Japan, Abs. 1929, **49**, 155). The mixture of suberic and azelaic acids obtained by the latter reaction may be separated by esterification with methyl alcohol and subsequent fractionation *in vacuo.* The acid may also be prepared from dihydroxystearic acid (Asahima and Ishida, *ibid.* 1922, **42**, 171) and by electrolysis of a mixture of potassium ethyl suberate and potassium ethyl malonate (Carmichael, J.C.S. 1922, **121**, 2545). Industrially it has been prepared by decomposition of oleic acid ozonide (D.R.P. 565158).

The acid crystallises in colourless plates, m.p. 106·2° (Massol, Bull. Soc. chim. 1898 [iii], **19**, 301) and exhibits dimorphism—slow evaporation of a cold solution yields an α-modification, whilst crystallisation from a hot saturated solution gives a β-modification; the two forms are, however, indistinguishable except by X-ray measurement (Caspari, J.C.S. 1928, 3235; 1929, 2709). It is readily soluble in alcohol but less soluble in water or in ether; its solubility in water is 0·10 parts per cent. at 0° rising to 2·2 parts per cent. at 65°. The dissociation constants found by Gane and Ingold (J.C.S. 1928, 1598) are $K_1\times10^5=2{\cdot}82$, $K_2\times10^6=4{\cdot}64$ (*see also* Bethman, Z. physikal. Chem. 1890, **5**, 401 ; Smith, *ibid.* 1898, **25**, 197 ; Wegscheider, Monatsh. 1902, **23**, 635 ; Voerman, Rec. trav. chim. 1904, **23**, 278 ; and Chandler, J. Amer. Chem. Soc. 1908, **30**, 713. For absorption spectrum data, *see* Grunfeld, Ann. Chim. 1933, **20**, 304).

Azelaic acid is conveniently characterised as its phenacyl ester, m.p. 69·7°, *p*-bromophenacyl ester, m.p. 130·6°, or *p*-phenylphenacyl ester, m.p. 141° (Kelly and Kleff, J. Amer. Chem. Soc. 1932, **54**, 4444 ; Drake and Sweeney, *ibid.* 2059). It may be estimated by potentiometric titration (Allard, Compt. rend. 1933, **196**, 937 ; Simms, J. Physical Chem. 1928, **32**, 1494 ; Ingold, J.C.S. 1928, 1594).

Distillation of salts of azelaic acid gives mixtures of cyclic ketones, *e.g. cyclo*-octanone, b.p. 205°, is obtained by heating azelaic acid with soda lime (Miller and Tschitschkin, Chem.

Zentr. 1899 [ii], 181) ; distillation of thorium azelate gives *cyclo*-hexanone, *cyclo*-octanone, *cyclo*-hexadecane-1 : 9-dione, nonan-*β*-one (*azelaone*), and *αω*-di-*n*-octoyl-*n*-heptane (Ruzicka, Brugger, Seidel, and Schinz, Helv. Chim. Acta, 1928, **11**, 496).

Derivatives.—*Esters.*—The *methyl* and *ethyl* esters are liquids, b.p. 156°/20 mm. and 148·7°/7·5 mm. respectively ; for other physical properties of the methyl ester, *see* Vogel (J.C.S. 1934, 333). *Ethyl hydrogen azelate*, m.p. 28°–29°, b.p. 178°–179°/5·5 mm., may be obtained by heating the diethyl ester with azelaic acid (Fourneau and Sabetay, Bull. Soc. chim. 1929, **45**, 834). *Azelayl chloride* has b.p. 165°/13 mm. and the *dinitrile* b.p. 183°/11 mm. The *anhydride*, m.p. 53°–55°, is obtained by heating azelaic acid with acetyl chloride or acetic anhydride (Etaix, Ann. Chim. Phys. 1896 [vii], **9**, 399 ; Hill and Carothers, J. Amer. Chem. Soc. 1933, **55**, 5023). For *αα′-dibromoazelaic acid* and its *ethyl ester*, *see* v. Braun and Münch (Ber. 1926, **59** [B], 1941) ; Challenor and Thorpe (J.C.S. 1923, **123**, 2483). For *αα′-dihydroxyazelaic acid*, *see* Goss and Ingold (*ibid.* 1926, 1471).

Resins may be obtained by condensing azelaic acid with glycerol (B.P. 348593 ; U.S.P. 1779367 ; F.P. 688962).

G. F. B.

AZELAONE *v.* Azelaic Acid.

AZIDES. The azides may be prepared generally by neutralising hydrazoic acid with hydroxides or carbonates or, preferably in the case of some of the heavy metals, by precipitating solutions of their salts with an alkali azide such as the sodium compound.

Many of the azides, especially those of the heavy metals, possess powerful detonating properties, but at present only the lead salt is used to any appreciable extent in the explosives industry.

Sodium azide (**NaN_3**) can be prepared by passing nitrous oxide over sodium amide at a temperature of 150°–250° C. It forms clear, colourless crystals having a sp.gr. of 1·846 at 20°C. It is easily soluble in water but somewhat sparingly soluble in alcohol. The salt is not hygroscopic or volatile and does not explode when struck with a hammer. When heated it melts without decomposition but detonates at a higher temperature.

Potassium azide forms tetragonal crystals which are readily soluble in water but only sparingly so in alcohol. It is not volatile or hygroscopic and when heated the salt melts and boils, nitrogen being given off. It does not explode when struck by a hammer.

Ammonium azide prepared by neutralising a solution of ammonia with hydrazoic acid, crystallises in colourless plates which are non-hygroscopic but distinctly volatile. On heating sublimation begins at about 100°C., and if rapidly heated it explodes.

Calcium azide forms colourless rhombic needles which are very hygroscopic and deliquescent. The salt does not explode by percussion but if rapidly heated decomposes violently. According to Wohler and Martin, explosion takes place at a temperature of 150°C.

Nickel azide is a green hygroscopic powder which is very soluble in water and rapidly hydrolyses. It is very sensitive to pressure, even gentle friction causing a violent explosion.

Cupric azide is prepared by mixing a dilute aqueous solution of copper sulphate and sodium azide, washing the precipitate with ice water and drying *in vacuo*. It is very explosive, even when moist and detonates readily either by friction or percussion.

Lead azide.—According to Hale (Army Ord. 1925–26, VI, 135), the general method employed for the manufacture of lead azide consists in treating a dilute aqueous solution of lead acetate with a weak solution of sodium azide. The reaction is carried out in a revolving drum or barrel, made of nickel, which is screened with a barricade. The required amount of lead acetate solution is first run into the drum and then the solution of sodium azide is gradually added while the drum is rotating at from 15 to 20 r.p.m. The lead azide, which separates in the form of extremely fine crystals, is removed by inverting the drum over a trough where the azide is washed repeatedly with cold water until neutral.

Properties.—Lead azide is more efficient, with regard to the amount required in effecting detonation, than fulminate of mercury ; 0·08 g. of the former being sufficient to detonate trotyl, whereas, under similar conditions of loading, etc., 0·35 g. of the latter is required. When finely divided it is less sensitive to shock than fulminate, a fall of 9 cm. for a 400 g. weight being necessary to cause explosion, whereas fulminate requires a fall of only 4 cm. Lead azide will function normally even when containing 5–10% water, but in the presence of both moisture and carbon dioxide it is liable to become non-explosive. It explodes at a temperature of 327°C., and the velocity of detonation is from 1,500 to 2,000 m./sec.

F. D. Miles (J.C.S. 1931, 2532), as the result of his investigations on the crystallography of lead azide, concludes that there are two crystalline modifications of this compound, both of which are anhydrous. The ordinary *α*-azide can be made by double decomposition without undue risk, although when large crystals are grown, by the cooling of hot saturated solutions, unexplained explosions may occur. The less stable or *β*-form shows a greater sensitiveness to causes of accidental explosion, and during its formation, by double decomposition, it is very liable to detonate. Lead azide may be crystallised from solutions of ammonium acetate or chloride, Rochelle salt or sodium acetate ; the best crystals, which were obtained from the latter solution, were about 2 mm. long and 1 mm. wide. Numerous experiments were necessary to obtain good specimens, as the crystals were usually ill-developed and often the products were lost in a violent explosion when the crystallisation was nearly complete. The material separated from the mother liquor was never unduly sensitive, however large the crystals might be from solution in ammonium acetate. It was possible to grow single, rather unevenly developed crystals of lead azide, which were 3 cm. or more in length, but which could be crushed to powder with a spatula without explosion. The widely held idea that large crystals of such explosive substances as lead azide are always excessively sensitive to shock or friction seems, therefore, in view of the above facts, to have little foundation.

β-Lead azide was prepared by slowly diffusing a solution of sodium azide in a lead nitrate solution. The crystals formed radiating clusters of thin needles, some of which were 4 cm. long. Under certain conditions the β-modification resulted from the simple mixing of the two solutions. When a 3·4% sodium azide solution was added to a 4% lead nitrate solution until a marked blue opalescence followed by a distinct turbidity was seen, the colloidal material disappeared after an hour and β-crystals were present. If the conditions are varied slightly from those given above α-material only may result, as the β → α-transition may be very rapid. The density of the β-crystals was found to be 4·93, whereas that of the α-modification was 4·71. When dry and protected from light the crystals of the β-azide remained unchanged for years. They may be heated in a vacuum for short periods without obvious change, but in water, or more rapidly in a solution of lead salt, they pass into the α-form by a process of solution and recrystallisation. Comparison by means of the fall-hammer method showed that the sensitiveness of the β-form was markedly higher than that of the α-modification.

Barium azide is extensively used in the manufacture of radio-valves. The anode plate is coated with the salt, the bulb is evacuated, and the plate heated by high frequency induction, the salt decomposes and some of the barium vapour is deposited on the cathode forming a so-called "oxide cathode," the remainder forms a metallic sublimate in the bulb, mixed with traces of oxide and nitride.

Mercurous azide.—The mercury salts of hydrazoic acid have been considered too dangerous to have practical importance, but B. Grotta (U.S.P. 1439099) states that mercurous azide can be prepared by methods which yield a comparatively safe product. It is claimed that mercurous azide, in contradistinction to lead azide, does not form the very sensitive copper azide when loaded into copper caps, and that it is practically unaffected by moisture and carbon dioxide. If mercurous azide is used in conjunction with fulminate of mercury in detonators the brisance of the latter is said to be greatly increased, and the mixture to be practically unaffected by moisture. Furthermore, mixtures containing 10–20% of mercurous azide and 90–80% fulminate are stated to retain the same ease of ignition as the latter material and not to become "dead pressed" under high pressures.

Silver azide.—According to Rinkenbach and Taylor (Army Ord. 1924–25, v, 824), silver azide is obtained in colloidal aggregates by mixing fairly concentrated solutions of silver nitrate and sodium azide. If dilute solutions are used, relatively large crystals are obtained.

Properties.—Freshly prepared silver azide is white in colour and remains unchanged if kept in the dark; if exposed to sunlight, however, it becomes cream-coloured. It is non-hygroscopic and only very slightly soluble in water, alcohol, ether, or acetone. The colloidal product melts at 251°C., and detonates at 273°C. It can be heated at 75°C. for some hours without undergoing any change, but above its melting-point it rapidly decomposes into silver and nitrogen. The product obtained from concentrated solutions is much less sensitive than that obtained when the reacting solutions are dilute, the former material requiring a fall of 777 mm. for a 500-g. weight to cause explosion, whereas for the latter a fall of only 285 mm. is required. Both forms are, however, less sensitive to blows than fulminate of mercury.

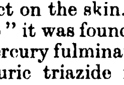
Silver azide is very effective as a detonating agent, only 0·05 g. being necessary to cause the detonation of trinitrotoluene under suitable conditions.

Cyanuric triazide (C_3N_{12}).—This compound, which was patented by E. Ott (U.S.P. 1390378), has been investigated by Taylor and Rinkenbach (U.S. Bureau of Mines Serial 2513), who prepared it by adding cyanuric chloride to a solution of pure sodium azide. The cyanuric chloride was disintegrated as much as possible under the solution, and the mixture allowed to stand for at least 12 hours to ensure completion of the reaction. The solid product was then filtered off, washed with distilled water, and dried.

Properties.—Cyanuric triazide is insoluble in water, but soluble in acetone, benzene, chloroform, ether or hot alcohol. It melts at 94°C. and decomposes when heated above 100°C. If heated slowly it may decompose completely without explosion, but detonation is brought about by contact with a flame or by sudden heating. The small crystals are more sensitive to impact and friction than mercury fulminate, and may detonate during pressing into detonator capsules. Large crystals have detonated when being crushed by means of a rubber-shod rod. Cyanuric triazide is non-poisonous and has no irritating effect on the skin. When tested in the "Sand Bomb" it was found to be much more powerful than mercury fulminate. As a detonating agent, cyanuric triazide is very effective, 0·1 g. being sufficient to detonate trinitrotoluene, whereas 0·26 g. of fulminate would be required under similar conditions. Although this material is very efficient as an initiatory explosive, it is considered to be too sensitive to handle safely in large quantities. H. S.

AZIDINE DYES *v.* DYESTUFFS, AZO.

AZIMINO COMPOUNDS. Cyclic diazoimines, *e.g.* aziminobenzene,



AZINES (Quinoxalines), Azonium Bases and Colouring Matters derived from them.

I. (*a*) **Azines.**—(i) *Introduction*; (ii) *Theory*; (iii) *Methods of Synthesis*; (iv) *General Properties*; (v) *Some Typical Examples.*

(*b*) **Dyestuffs derived from Azines.**—Classification and Methods of Synthesis.—(A) *Eurhodines*; (B) *Eurhodols*; (C) *Some Examples.*

II. Azonium Bases and Derived Dyestuffs.—(*a*) (i) *General Considerations*; (ii) *Structure*; (iii) *Methods of Synthesis*; (iv) *Structure of Azonium Dyestuffs* (continued).

(*b*) *Monoamino* (or *Hydroxy*) *Derivatives* (*iso*- and apo-safranines, *iso*-rosindulines).

(*c*) *Diamino Derivatives* (safranines, phenosafranines, tolusafranines, naphthasafranines, mauveine, indazine).

III. Miscellaneous.

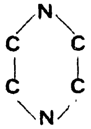
IV. Indulines (*see* INDULINES).

V. Nigrosines (*see* NIGROSINES).

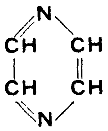
VI. Literature.

I. (*a*) AZINES.

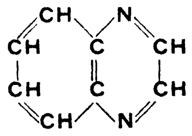
(i) Introduction.—The term *Azines* has been given to a group of organic bases containing as the essential structure a six-membered heterocyclic ring consisting of four carbon atoms with two nitrogen atoms in the 1 : 4 positions:



The name *Azine* is not very well chosen, as it might lead to confusion with other types of compounds such as the hydrazines, and the proposal has been made to use the name *Diazine*. Thus the simplest member of the group:



is known as 1 : 4-*Diazine* or *Pyrazine*. The term *Quinoxaline* was suggested by Hinsberg but is now limited to bodies of the structure:



The name *Azine* is, however, now so well established that it is unlikely to lead to misunderstanding, particularly in connection with the azine and azonium group of dyestuffs with which we are here specially concerned (*see* Meyer and Jacobson, "Lehrbuch der organischen Chemie," III, (3), pp. 1146–7, 1348 *et seq.*, 1376 (Berlin, 1920)).

The name *Azonium bases* was given by Witt to the class of organic bases derived from the azines by the attachment of an aromatic radical to one of the nitrogen atoms which passes from the trivalent to pentavalent condition, with marked change in the properties of the resultant substance.

Both the azines and the azonium bases are powerful chromogens. Being strongly basic and capable of assuming a quinonoid structure, they possess some characteristics of dyestuffs which, however, become more strongly developed by the introduction of suitable auxochromes, mainly amino-groups. A large number of powerful colouring matters have thus been obtained, some of which are, or have been, of considerable practical importance. Mauveine, or Perkin's Violet, the earliest forerunner of the synthetic dye industry, belongs to the group of azonium dyes.

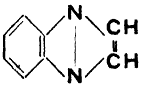
The constitutions of most of the members of the group have now been established by researches of Witt, Nietzki, Otto Fischer, Hepp and notably Friedrich Kehrmann, and the group includes such well-known types as the eurhodines, eurhodols, safranines, safranols, apo-safranines, indulines, nigrosines, fluorindines and aniline black.

The first eurhodines were prepared in 1879–1885 by Witt, who recognised them as belonging to a new class of dyestuffs related to the safranines, and showed that they are amino derivatives of the azines; he also isolated the first eurhodol. As a result of this work the nature and structure of the safranines was elucidated as diamino derivatives of their hypothetical azonium bases, Nietzki and Bernthsen arriving simultaneously at the same conclusion.

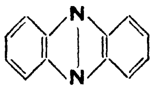
The typical safranines and indulines were discovered in the early days of the synthetic dye industry by empirical methods, Perkin's mauve being isolated in 1856, and phenosafranin by Witt in 1877.

(ii) Theory.—The simplest azine, *pyrazine* (or 1 : 4-diazine), $C_4H_4N_2$, is unimportant but its substitution products, in which the hydrogen atoms are replaced by organic radicals, form the large group of the ketine or aldine bases. These exhibit no colour nor do they form any derivatives having the characters of dyestuffs; pyrazine and the ketines are not therefore now generally considered as belonging to the azine group proper, and will not be dealt with further here.

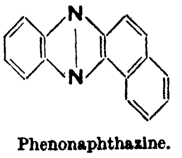
The characteristic properties of the azines only appear in compounds in which at least one other ring system is fused on to the pyrazine ring, thus:



Phenazine.

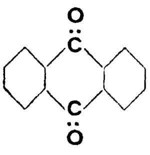


Diphenazine.

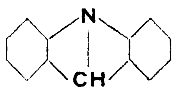


Phenonaphthazine.

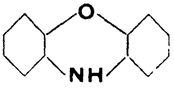
The true azines are thus named according to the nature of the fused aromatic ring; they show close analogies with other polycyclic and heterocyclic ring systems, such as:



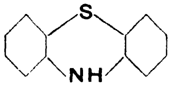
Anthraquinone.



Acridine.



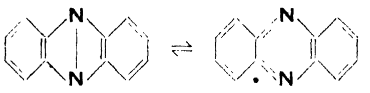
Oxazine.



Thiazine.

which are well-known chromogens.

Regarding the possible structural formulæ for diphenazine, there are two alternatives:



I. II.

Formula I was proposed by Claus for his "azophenylene" (Annalen, 1873, **168**, 1), and by Merz for his azines (Ber. 1886, **19**, 725), whilst II was put forward by Hinsberg for his quinoxalines (Ber. 1884, **17**, 319). Formula I explains by its symmetry the great stability of the azines, which may be distilled unchanged at relatively high temperatures, whilst formula II agrees better with some of the chromogenic properties.

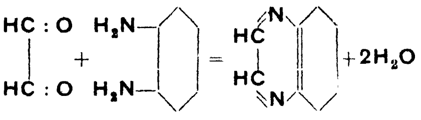
It is now generally assumed that the azines are tautomeric substances and that in the free state, where they are volatile and colourless, they possess the symmetrical (azine) structure I, whilst the strongly coloured salts may be regarded as being derived from the *ortho*-quinonoid form II.

In the colouring matters derived from the azines the problem is further complicated by the fact that the auxochromic groups also participate in the formation of a quinonoid structure, which may be either *ortho-* or *para*-quinonoid. This question is discussed more fully in sections II (*a*), (ii) (p. 570), and (iv) (p. 574), when dealing with the structure of the azonium dyes.

(iii) **Methods of Synthesis.**—(1) By heating *a*-nitronaphthalene with quicklime (Laurent, Ann. Chim. Phys. 1860 [iii], **59**, 384; Doer, Ber. 1870, **3**, 291; Klobukowski, *ibid.* 1877, **10**, 573) dinaphthazine is formed; the quicklime may be replaced by zinc dust or lead oxide.

(2) Diphenazine is formed in considerable quantities on heating nitrobenzene with strong aqueous caustic soda, or with barium oxide (Zerewitinoff and Ostromisslenski, Ber. 1911, **44**, 2402); it may also be obtained by dry distillation of the calcium or potassium salt of *o*-azobenzoic acid (Claus and Rasenack, Annalen, 1873, **168**, 1).

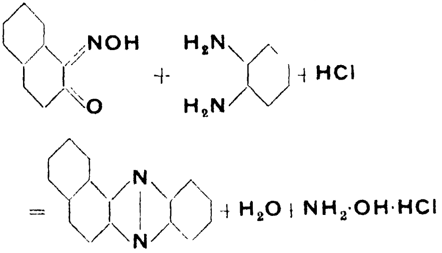
(3) A general method is that of Hinsberg (Ber. 1884, **17**, 319; 1885, **18**, 1228) and Körner (Ber. 1884, **17**, Ref. 573), who showed that when an *alpha-* or *o*-diketone reacts with an aromatic *o*-diamine two molecules of water are eliminated with formation of an azine, *e.g.*:



Glyoxal *o*-Phenylene-diamine. Phenazine (quinoxaline).

This reaction affords one of the best methods of identifying an *ortho*-diamine or an *ortho*-diketone; only small quantities of the components are necessary and the resultant azine is easily recognised by its melting-point and by its colour reaction with sulphuric acid.

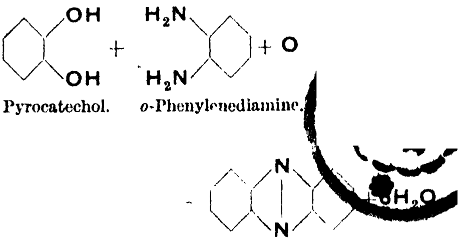
Hinsberg's method may be extended to nitroso-*β*-naphthol, which reacts as the oxime of 1:2-naphthaquinone. Thus, naphthaphenazine is obtained by heating *o*-phenylenediamine hydrochloride with nitroso-*β*-naphthol:



Naphthaphenazine.

(Ullmann and Heisler, Ber. 1909, **42**, 4263).

(4) Merz's method consists in condensing *o*-dihydroxy derivatives with *o*-diamines and air oxidation of the products, *e.g.*:

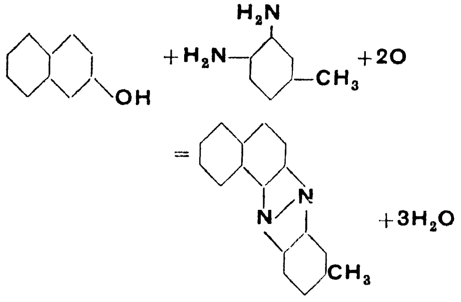


Pyrocatechol. *o*-Phenylenediamine. Diphenazine.

(5) Diphenanthrazine may be obtained by heating phenanthraquinone with ammonia or, better, ammonium acetate. In the same way *β*-naphthaquinone affords dinaphthazine.

(6) Another general method consists in the joint oxidation of a phenol (containing an already substituted *para*-position) and aromatic *o*-diamines; thus, *β*-naphthol and 1:3:4-

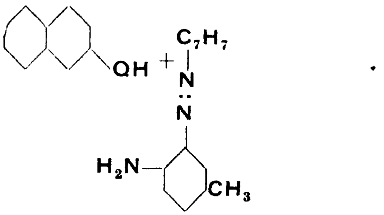
tolylenediamine on oxidation together, yield tolunaphthazine.



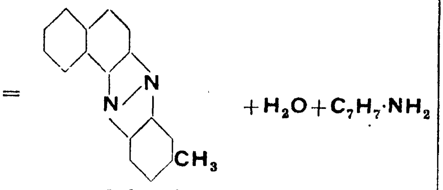
Tolunaphthazine.

(Witt, Ber. 1886, 19, 917).

(7) By heating *β*-naphthol with *o*-aminoazotoluene the same tolunaphthazine may be obtained, the azo group removing the hydrogen and forming the necessary diamine.



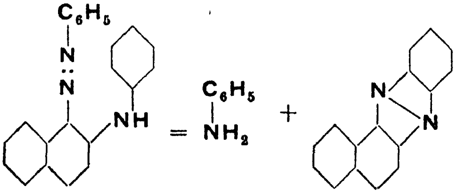
o-Aminoazotoluene.



Tolunaphthazine.

(Ullmann and Ankersmit, Ber. 1905, **38**, 1811).

(8) A somewhat similar method is that of Witt (Ber. 1887, **20**, 571), who showed that the *ortho*-azo derivatives of secondary amines (more especially those amines containing the *β*-naphthyl group) are decomposed by being heated with acids into the corresponding azine and amino-compound. The reaction works smoothly and usually affords excellent yields: in effect it is a condensation of the secondary amine to the corresponding azine by the dehydrogenating influence of the azo-group temporarily introduced for that purpose:



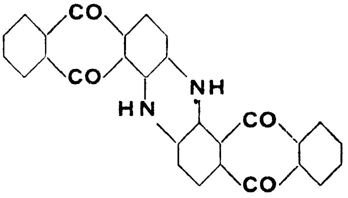
Benzene-azo-phenyl-*β*-naphthylamine. Aniline + Naphthaphenazine.

(9) Diphenazine may also be obtained by heating *o*-nitraniline with *o*-nitrobromobenzene, in presence of cuprous chloride (Eckert and Steiner, Monatsh. 1914, **35**, 1153).

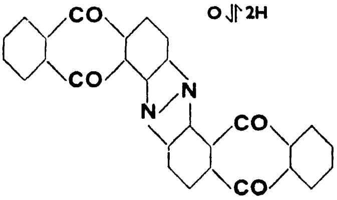
(iv) **General Properties.**—The azines are in general white, pale yellow or occasionally orange crystalline solids of great stability. They have high melting-points and boil at atmospheric pressure at very high temperatures (sometimes approaching a red-heat) almost without decomposition. At temperatures below their boiling-points they sublime, the vapours condensing to voluminous aggregates of crystals. All the azines are bases, forming coloured salts with acids. The mono-acid salts with mineral acids may usually be obtained in crystalline condition but are stable only in absence of water or in excess of acid ; water readily hydrolyses them into acid and free base. The salts are intensely coloured, which may be taken as an indication that they contain the base in the quinonoid form which reverts to the symmetrical form on hydrolysis. The di-acid salts cannot be isolated, the evidence for their existence being furnished by the intense red, violet and blue colorations shown by solutions of the azines in a large excess of strong acid, preferably sulphuric acid. On dilution with water the diacid salt is decomposed, the yellow or orange mono-acid salt is formed and on further addition of a large excess of water the free azine itself separates These striking colour reactions afford the best means of identifying the bases.

The azines, however, are not applicable as dyestuffs and may only be regarded as chromogens which are capable of producing colouring matters on the further introduction of auxochromic groups, in analogy with the other heterocyclic chromogens of the acridine, oxazine and thiazine groups.

There is one very large and technically important group of azines to which the above general remarks do not apply; these are the azines of the anthraquinone group such as that derived from Indanthrene Blue R, the actual dye being the dihydro derivative. These form an important group of vat dyes, often of very considerable fastness and consideration of these

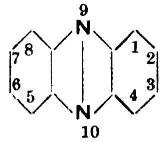


Indanthrene Blue R.



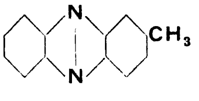
is reserved for a special article (*see* ANTHRAQUINONE DYESTUFFS, p. 411).

(v) Some Typical Examples of Azines.—*Diphenazine*, $C_{12}H_8N_2$,



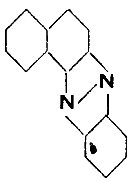
m.p. 170°–171°. Soluble in alcohol and other organic solvents, b.p. above 360°C., without decomposition, forms unstable yellow and red salts in excess of strong acids (*cf.* Meyer-Jacobson, Lehrbuch d. org. Chemie, II [iii], p. 1392 (1920)). (Literature very considerable.)

Toluophenazine, $C_{13}H_{10}N_2$,

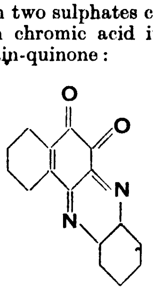


from pyrocatechol and *o*-tolylenediamine, m.p. 117°, b.p. 350°C., has properties similar to those of diphenazine.

Naphthaphenazine, $C_{16}H_{10}N_2$,

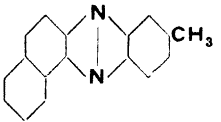


prepared by the action of acids upon azo-compounds of phenyl-*β*-naphthylamine, or from *β*-naphthaquinone and *ortho*-phenylene diamine, forms yellow needles, m.p. 142·5°C., sublimes about 200°, b.p. above 360°C., dissolves in sulphuric acid with a reddish-brown coloration from which two sulphates crystallise out on dilution. With chromic acid it is oxidised to naphthophenazin-quinone:



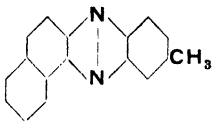
m.p. 265°C.

Tolunaphthazines, $C_{17}H_{12}N_2$. Two isomers of this formula are known, containing a methyl group in the phenyl nucleus, melting at 179·8°C. and 169°C. respectively. The former, I, from *o*-tolylenediamine and *β*-naphthol, gives a violet coloration in sulphuric acid; the latter, II, from the azo-derivatives of *para*-tolyl-*β*-naphthylamine, gives a reddish-brown coloration in sulphuric acid.



I.

Tolunaphthazine, m.p. 179·8°C.

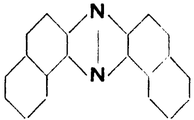


II.

Tolunaphthazine, m.p. 169°C.

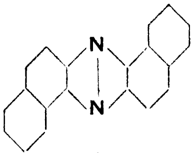
A third tolunaphthazine described by Hinsberg as melting at 139°–142° (Annalen, 1887, **237**, 343 (*a*), 371) consists of a molecular compound of the other two.

Dinaphthazines, $C_{20}H_{12}N_2$. Of the numerous possible isomeric dinaphthazines three are known.



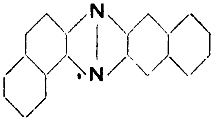
I.

Sym. *α* : *β* : *α′* : *β′*-dinaphthazine (1 : 2 : 7 : 8-dibenzophenazine).



II.

Unsym. *α* : *β* : *α′* : *β′*-dinaphthazine (1 : 2 : 5 : 6-dibenzophenazine).



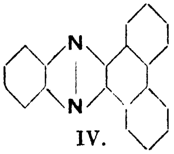
III.

lin. *α* : *β* : *β′* : *β′*-dinaphthazine (1 : 2 : 6 : 7-dibenzophenazine).

I may be prepared from benzeneazo-*β* : *β′*-dinaphthylamine, $Ph{\cdot}N_2{\cdot}C_{10}H_7{\cdot}NH{\cdot}C_{10}H_7$, by warming with hydrochloric acid in acetic acid, and is indeed readily formed even on adding a strongly acid aqueous solution of benzene diazonium chloride to a warm solution of *β*-*β′*-dinaphthylamine. It melts at 242–3°C. and is the parent substance of certain commercial dyestuffs. III is prepared from *β*-naphthaquinone and 2 : 3-diamino-naphthalene and melts at about 247°C.

II is the best known of the isomers and was first obtained in 1835 by Laurent (under the name of "Naphthalase") on heating *α*-nitronaphthalene with quicklime. It may also be obtained readily on melting *β*-naphthylamine with potash. It forms yellow needles, m.p. 284°C., dissolves in strong sulphuric acid with a deep violet colour turning orange-yellow on dilution and depositing the free base.

Phenanthraphenazines, $C_{20}H_{12}N_2$. Owing to the ease with which phenanthraquinone reacts with all *ortho*-diamines to form well-crystallised azines with definite melting-points, it is very frequently used for identifying *ortho*-diamines. The azine IV:



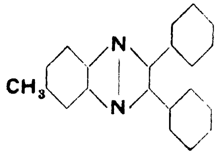
IV.

from *o*-phenylenediamine and phenanthraquinone, forms pale yellow needles, m.p. 217°, and affords a bright red colour in conc. sulphuric acid. The corresponding compound from *o*-tolylenediamine has m.p. 212°–213°.

Phenanthranaphthazine, $C_{24}H_{14}N_2$, from 1 : 2-naphthylenediamine and phenanthraquinone, has m.p. 273°, and gives a violet coloration in sulphuric acid (Lawson, Ber. 1885, **18**, 2426).

Chrysotoluazine, $C_{25}H_{16}N_2$, and *Chrysonaphthazine*, $C_{28}H_{16}N_2$, have also been prepared by Liebermann and Witt (Ber. 1887, **20**, 2442).

Tolustilbazine, $C_{21}H_{10}N_2$,



V.

from benzil and *o*-tolylenediamine, has m.p. 111°, and gives a crimson solution in sulphuric acid (Hinsberg, Annalen, 1887, **237**, 339).

I. (*b*) DYESTUFFS DERIVED FROM AZINES.

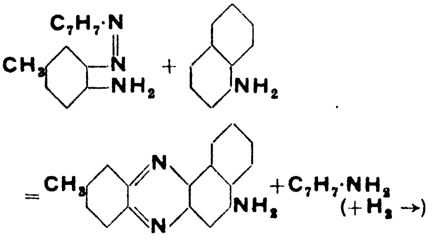
Classification and Methods of Synthesis.—By the introduction of suitable auxochromic groups, notably $-NH_2$ or $-OH$, the azines yield colouring matters known respectively as *Eurhodines* (containing one or more amino groups) and *Eurhodols* (containing hydroxyl groups).

Like the parent substances the eurhodines and eurhodols give characteristic colorations in strong mineral acids which change on dilution with water. The substances act as red to violet dyes.

The following general methods of production may be noted.

(A) Eurhodines.

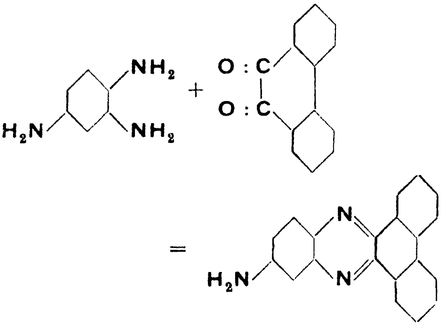
(1) By heating together any *ortho*-aminoazo compound with the hydrochlorides of certain aromatic mono-amines such as *a*-naphthylamine, preferably in phenol solution (Witt, Ber. 1883, **18**, 1119 ; 1884, **19**, 441). By this means *eurhodine* is formed from 4-amino-*m*-azo-toluene and *a*-naphthylamine hydrochloride :



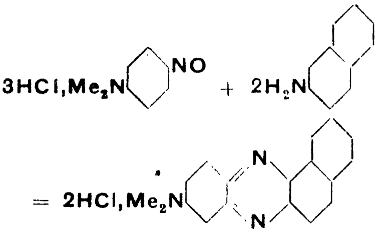
Eurhodine.

In this reaction an *ortho*-diamine is first formed (by reduction of the aminoazo compound), which then unites with the *a*-naphthylamine with elimination of hydrogen and reduction of a further quantity of the aminoazo compound. The first eurhodine was discovered by Witt by this method (*l.c.*). The lower homologue is formed from phenylenediamine and benzene-azo-*a*-naphthylamine (Fischer and Hepp, Ber. 1890, **23**, 846, 2788).

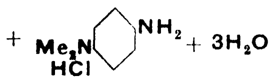
(2) Another general method consists in bringing together an *a*-diketone with an aromatic triamine containing two amino groups in the *ortho*-position. Thus, phenanthraquinone and 1 : 2 : 4-triaminobenzene afford a eurhodine :



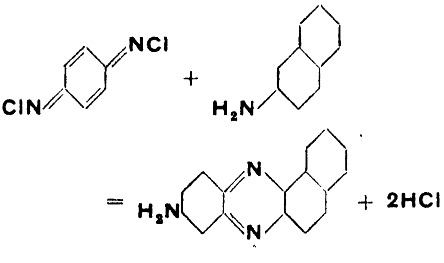
(3) Another method of wide applicability consists in heating together nitrosoamines or quinone-dichloroimides with aromatic amines containing a para-substituent. For instance, the eurhodine, dimethylaminophenonaphthazine, may be obtained by heating together nitrosodimethylaniline hydrochloride and *β*-naphthylamine in acetic acid solution :



Dimethylaminophenonaphthazine hydrochloride.



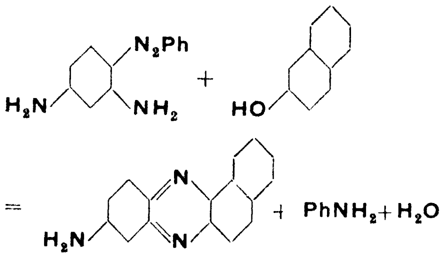
and on substituting the nitrosodimethylaniline by dichloroquinoneimide, aminophenonaphthazine is formed :



(Witt, Ber. 1888, **21**, 719 ; Nietzki and Otto, *ibid.* 1598).

(4) Eurhodines may also be obtained by the reduction (with ammonium sulphide) of nitro-azines ; nitrophenophenanthrazine, for example, yielding the eurhodine, aminophenophenanthrazine.

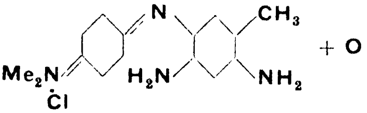
(5) Certain azo dyes such as chrysoidine on heating with β-naphthol yield a eurhodine:



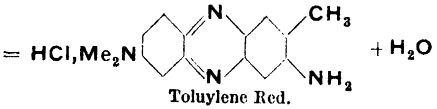
(Ullmann and Ankersmit, Ber. 1905, **38**, 1812).

The above methods afford mono-amino phenazines which are for the most part of no technical value. Certain diamino-phenazines, however, have attained to a moderate degree of success as commercial dyestuffs, though their uses are now very limited.

(6) Thus, diaminoazines are formed on prolonged boiling of solutions of certain indamines: "Toluylene Blue" (the indamine from nitrosodimethylaniline and *m*-tolylenediamine, "Colour Index," No. 820), on boiling for some time in solution, yields *Toluylene Red* ("Colour Index," No. 825).



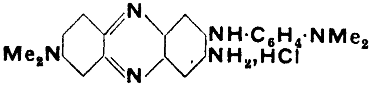
Toluylene Blue.



Toluylene Red.

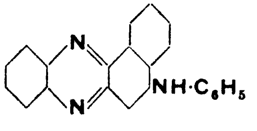
(7) Di- and polyamino-azines may also be prepared by the oxidation of *ortho*-diamines and of polyamines containing two amino groups in the *ortho*-position (Fischer and Hepp, Ber. **22**, 355; Nietzki and Müller, Ber. 1889, **22**, 447).

Of other polyamino-phenazines there may be mentioned *Neutral Violet* ("Colour Index," No. 826).



Nigrosine or *Methylene Grey* is probably of a similar type and is formed as a by-product in the manufacture of Gallamine Blue or of Gallocyanine.

Green azine dyes of the type



have been prepared by Bayer & Co. from 1:3-**diarylnaphthylenediamines** or their sulphonic acids (G.P. 230456).

(B) Eurhodols.

(i) Sulphonic acids of azines on fusing with potash yield the corresponding eurhodols.

(ii) Some eurhodines afford the corresponding eurhodols on replacement of the amino groups by hydroxyls when heated under pressure with strong acids.

(iii) Diazotised eurhodines on boiling with water yield the eurhodols, whilst with alcohol the corresponding alkyl ethers are formed.

(C) Some Examples.—The eurhodols have no technical value and of the eurhodines only Toluylene Red (Neutral Red, "Colour Index," No. 825) and Neutral Violet ("Colour Index," No. 826) have attained to any commercial importance.

Typical Eurhodines.—α-Aminonaphthatoluazine, first prepared by Witt (J.C.S. 1886, **49**, 391) by heating to 130° equal molecular quantities of 4-amino-*m*-azotoluene (m.p. 118·5°) and α-naphthylamine hydrochloride dissolved in phenol, the colour of the mixture changing from emerald green to scarlet. On the addition of toluene to the melt the hydrochloride of the eurhodine is precipitated and is then recrystallised from dilute hydrochloric acid. The free base may be liberated by the action of ammonia or alkalis, as a yellow powder which crystallises from aniline as yellow prisms or brown needles. In ether it affords a yellow solution with the strong green fluorescence characteristic of this type of dyestuff.

Eurhodine forms three series of salts, of which, however, only the mono-acid salts are stable to water. Its solution in strong sulphuric acid has a cherry-red colour; on addition of a little water the colour changes to emerald green and on further dilution the brilliant scarlet of the normal sulphate is obtained. This colour change is typical of the eurhodines, the parent azines and the safranines.

The well-crystallised eurhodine salts are of a bronzed copper colour and dissolve in water to a scarlet solution from which mordanted cotton is dyed in bright red shades. The dyeings are however, loose to washing and gradually turn yellow due to formation of the free yellow base.

Aminophenonaphthazine, $C_{16}H_{11}N_3$, forms crimson normal salts. On diazotisation and boiling with alcohol the ordinary phenonaphthazine is obtained, m.p. 142·5°.

Dimethylaminophenonaphthazine, $C_{18}H_{15}N_3$. The free base, m.p. 205°, forms fine scarlet crystals from xylene solution, which resemble magnesium platinocyanide. Colour change in sulphuric acid, violet → black → green → violet.

Aminophenophenanthrazine, $C_{20}H_{13}N_3$, forms short yellow prisms from toluene, m.p. 279°.

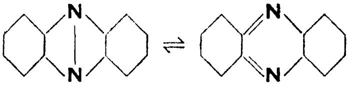
Dimethylaminopheno-aminotoluazine, *Toluylene Red*, $C_{15}H_{16}N_4$.—This dye forms orange crystals containing four mols. water of crystallisation, which are lost at 150°, leaving the anhydrous base as a dark red powder. The hydrated base is soluble in ether to a pink solution with a fine orange fluorescence. Colour change in sulphuric acid, green → sky-blue → red. The normal mono-acid salts dye mordanted or unmordanted cotton in pink to copper-red shades of poor fastness; it has been used to a small extent in calico printing.

Typical Eurhodol, α-hydroxynaphthatoluazine, $C_{17}H_{11}N_2{\cdot}OH$, forms yellow-red leaflets soluble in concentrated sulphuric acid to a red solution. In aqueous caustic soda it dissolves to an orange solution.

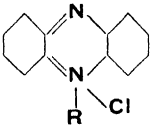
Eurhodol, α-hydroxynaphthaphenanthrazine, $C_{24}H_{14}N_2{\cdot}OH$, forms intense indigo-blue solution in sulphuric acid, changing to red on addition of water. It dyes alum-mordanted cotton in yellow shades, but is devoid of commercial importance.

II. (a) AZONIUM BASES AND DERIVED DYESTUFFS.

(i) General Considerations.—By the addition of an alkyl or more usually an aryl radical to one of the nitrogens of the phenazine molecule a new type of compound is obtained which forms the base of a number of dyestuffs of theoretical and practical importance :



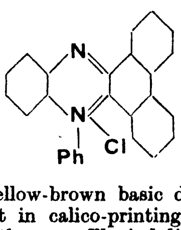
Diphenazine.



N-Alkyl (or aryl) Diphenazonium Chloride.

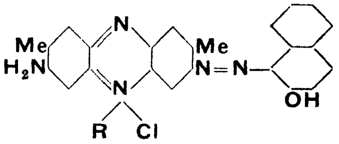
Included amongst these are some of the earliest synthetic dyes, such as Mauveine, Safranine, Rosinduline, etc., and though their practical importance has been much diminished by the introduction of more modern and faster dyestuffs, they still occupy an honoured and important position in the dyestuff industry.

As already mentioned, the phenazonium salts themselves are not dyestuffs, but become so on the addition of suitable auxochromic groups, usually amino (or substituted amino) groups, less frequently hydroxyl. An exception to this is phenyl-phenanthraphenazonium chloride :



which is a yellow-brown basic dye used to a limited extent in calico-printing and leather-dyeing under the name *Flavinduline O* ("Colour Index," No. 824).

The azonium dyes bear some resemblances in character to the triphenylmethane colours. The amino derivatives are usually red to violet, whilst the arylamino derivatives are generally violet to blue, or even bluish-green. In the case of diamino derivatives one — NH_2 can be readily diazotised and coupled with suitable amine or phenolic components, *e.g.* *Janus Blue G* ("Colour Index," No. 135), which has the composition Safranine-azo-β-naphthol.

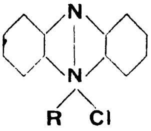


Janus Blue G.

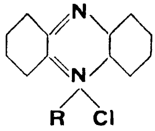
The second or third amino groups, however, can only be diazotised with difficulty, in concentrated acid. The azonium dyestuffs are normally basic, but may be sulphonated to yield acid colours.

(ii) Structure.—All the dyestuffs of this group, the *Aposafranines*, *Safranines*, *Rosindulines*, etc., are considered to be amino derivatives of azonium bases, to which they stand in the same relation as the eurhodines to the azines, the corresponding hydroxy derivatives being termed *safranols*.

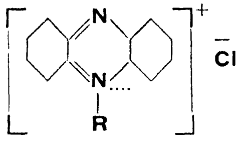
In the case of the unsubstituted azonium bases there are two (or perhaps three) possible modes of formulation, *e.g.* the bridged formula I,



I.



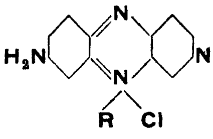
II.



III.

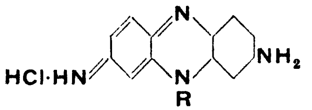
the *ortho*-quinonoid formula II, and its modern version based on Werner's co-ordination theory III (*cf.* Kehrmann, Helv. Chim. Acta, 1922, **5**, 71). Formula I is not generally adopted to-day by chemists, and whilst III has much in its favour from the purely theoretical point of view, as a matter of practical convenience the simpler formula II is generally adopted (*cf. also* Köchlin and Fierz-David, Helv. Chim. Acta, 1918, **1**, 211).

In the case of the phenazonium dyestuffs, however, the matter is further complicated by the fact that the presence of one (or more) amino groups offers the possibility of a *para*-quinonoid constitution in addition to *ortho*-quinonoid (*see below*), and the problem has led to a large volume of research by Kehrmann, Bernthsen, Witt, Nietzki and others :



Ortho-quinonoid,

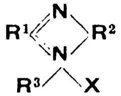
and



Para-quinonoid.

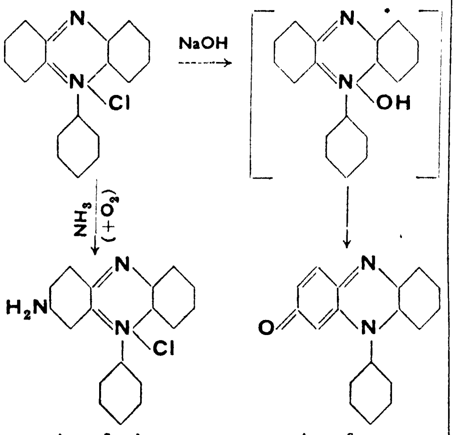
This matter is discussed in more detail on p. 574.

The azonium bases themselves stand in the same relation to the azines as the ammonium bases to the amines, but have not been obtained in analytically pure form. The general constitution of the azonium compounds may be expressed by the structural formula IV :



IV.

in which **R**^{1} and **R**^{2} are aromatic radicals (phenylene, naphthylene, etc., generally substituted), and **R**^{3} is an aliphatic or aromatic radical and **X** is an acidic group (or hydroxyl). The azonium bases possess strongly basic properties resembling the ammonium bases ; they are, however, unstable, since on treating, for instance, phenyl-phenazonium chloride with caustic soda we do not obtain the free base itself but a quinone, ***safranone*** (***aposafranone***), whilst with ammonia the chloride yields at once phenylaminophenazonium chloride or ***aposafranine*** :



Aposafranine. **Aposafranone (m.p. 248°–249°).**

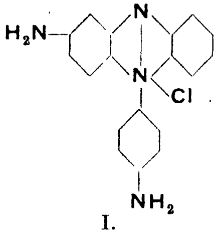
(*cf.* Kehrmann and Schaposnikow, Ber. 1896, **29**, 2316).

This unusual method of amination is of importance both scientifically and technically and affords an explanation of the mode of formation of certain more complex azonium compounds such as the ***Indulines*** and ***Nigrosines*** (*q.v.*).

The azonium bases and derived dyes are very strongly coloured, but only become useful dyestuffs on the introduction of amino groups into the molecule. The number of theoretically possible safranines is very large, and Kehrmann and his pupils have prepared a great variety of isomers.

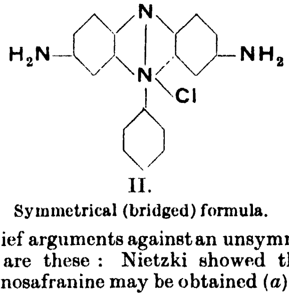
Only a minority of the known safranines are mono-amino derivatives of azonium bases, some are of unknown or doubtful constitution, but the majority are unsymmetrical diamino derivatives containing an amino (or substituted amino) group attached to nuclei R^1 and R^2 (*v.* IV).

The constitution of phenosafranine and related azonium dyes was recognised by Witt, who pointed out the analogy between the eurhodines and the safranines (Ber. 1885, **18**, 1119 ; 1886, **19**, 446) and considered the latter to be salts of unsymmetrical diamino-azonium bases (*ibid.* 3121) (I). Bernthsen and other chemists, however (*ibid.* 2690), preferred a symmetrical mode of formulation (II) :



I.

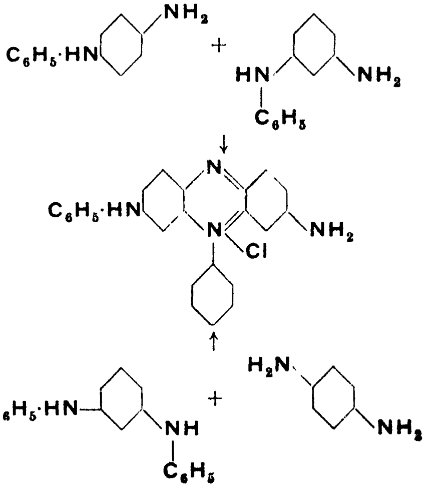
Witt's unsymmetrical formula.



II.

Symmetrical (bridged) formula.

The chief arguments against an unsymmetrical formula are these : Nietzki showed that the *same* phenosafranine may be obtained (*a*) by condensing phenyl-*m*-phenylenediamine with phenyl-*p*-phenylenediamine, or (*b*) from diphenyl-*m*-phenylenediamine (= *m*-aminophenyl diphenylamine) and *p*-phenylenediamine :

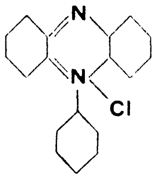


a result that cannot easily be explained on the assumption of an unsymmetrical formula.

Again, the synthesis of safranine from *m*-aminodiphenylamine and *p*-phenylenediamine also affords evidence for the symmetrical formula, since a safranine is also produced if methyl-*m*-phenylene diamine be used in place of phenyl-*m*-phenylenediamine, a result clearly incompatible with an unsymmetrical formula, for whilst the methyl group can replace the phenyl group attached to the azonium nitrogen atom, it cannot possible replace one of the benzene nuclei of the azine ring system as would be required by the unsymmetrical formula.

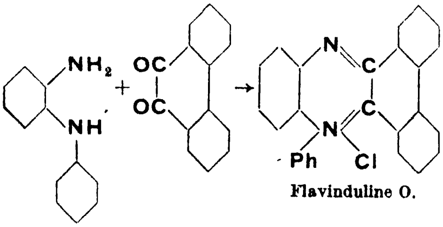
Claims to have obtained two isomeric forms of safranines have been made by Nietzki and also by Barbier and Sisley (Ann. Chim. Phys. 1908 [viii], **13**, 96), but later investigators have shown the two alleged isomers to be in fact identical (*cf.* Körner and Schraube, Chem.-Ztg. 1893, **17**, 305 ; Hewett, Newman and Winmill, J.C.S. 1909, **95**, 577 ; Havas and Bernhard, Ber. 1913, **46**, 2723). The balance of evidence is therefore definitely in favour of the accepted symmetrical formula for safranine and related dyestuffs (*see also* Kehrmann and Klopfenstein, Ber. 1923, **56** [B], 2935 ; Kehrmann and Listiva, Helv. Chim. Acta, 1925, **8**, 655 ; Kehrmann and Stanoyevitch, *ibid.* 661, 663 ; Kehrmann and Safar, *ibid.* 608 ; Kehrmann and Haening, *ibid.* 675).

Azonium Bases.—(1) Phenylphenazonium chloride was obtained by Kehrmann by diazotising mono-aminophenylphenazonium



chloride in concentrated sulphuric acid and then treating the green solution with alcohol. It forms brilliant reddish-brown prisms or needles, m.p. 186°C.

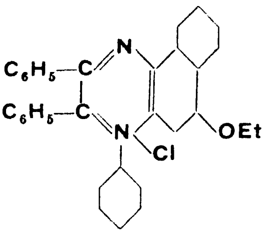
(2) By condensing phenyl-*o*-phenylenediamine with phenanthraquinone in acetic acid solution and adding a mineral acid there is obtained the yellow basic dye *Flavinduline O.*



Flavinduline O.

The hydrochloride, hydrobromide, and hydroiodide of Flavinduline are described by Yamada and Noguchi (J. Soc. Chem. Ind. Japan, 1935, **38**, 134).

(3) A similar brilliant yellow basic dye was obtained by Witt and Schmidt (Ber. 1892, **25**, 1013), from benzil and 1-ethoxy-3-phenylamino-4-aminonaphthalene :



Phenyl-ethoxynaphthastilbazonium chloride.

It is too costly, however, for practical use.

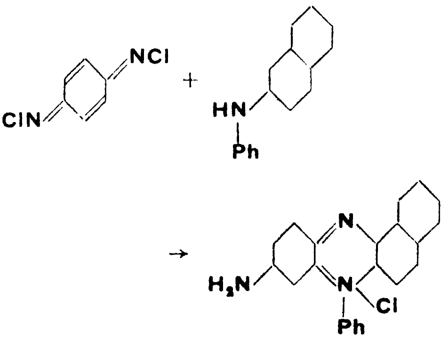
Whilst it is convenient for purposes of classification to divide the azonium dyestuffs into two main groups according to whether one or more amino groups are present as auxochromes, the actual methods of production are similar in the two cases and are here considered together.

(iii) **Methods of Synthesis.**

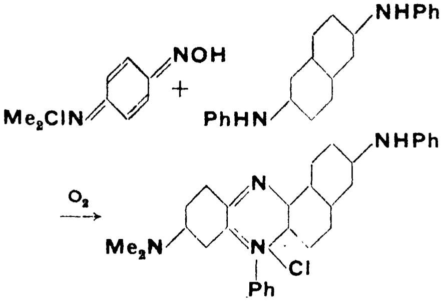
(1) Reduction of nitro-derivatives of azonium bases : thus nitrophenanthraquinone may be condensed with naphthylene-monophenyldiamine and the resultant nitro compound reduced to a reddish-violet safranine.

(2) On heating the ethoxy stilbazonium base obtained by Witt and Schmidt (*v.s.*) with ammonia, the ethoxy group is replaced by an amino group, yielding a safranine.

(3) By the action of dichloroquinone-imides upon secondary aromatic amines (in which the *para*-position to the amino group is occupied), monoamino-azonium bases are formed. For instance, dichloroquinone-imide and β-phenylaminonaphthalene react thus :

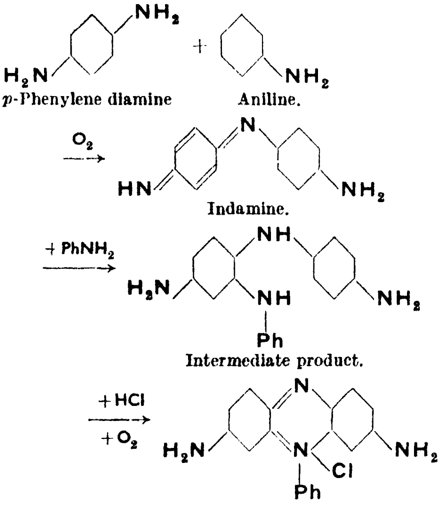


(4) In a similar manner *para*-nitrosodimethylaniline (or other *p*-nitroso amine) will react with suitable bases to yield safranines ; thus with 2 : 6-naphthylenediphenyldiamine it yields *Azine Green GB* ("Colour Index," No. 834).



Azine Green GB.

(5) The safranines proper are formed by the joint oxidation of one molecule of a diamine and two molecules of an aromatic monoamine; indamines are formed as intermediate products in the process. This is the general method used for the production of safranines :



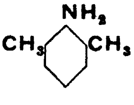
p-Phenylene diamine Aniline.

Indamine.

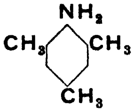
Intermediate product.

Safranine B (Phenosafranine).

Other *para*-diamines may also be used and various mono-amines may replace aniline, but the *para*-position in the amine must, of course, be unoccupied, and also one of the *ortho*-positions must be free. Thus indamines of the above type will form safranines with all usual primary amines of the benzene series, with the exception of the xylidine and mesidine of the formulæ :



Xylidine.



Mesidine.

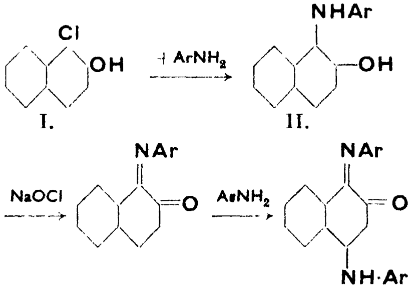
as these have no free *ortho*-positions available for the formation of the azonium groups (Nietzki, Ber. 1886, **19**, 3017, 3136).

It is also necessary for the second monoamine to be a primary base, whilst the amine used for forming the indamine may be primary, secondary, or tertiary, provided the *para*-position is free.

The oxidation may be effected conveniently with chromic acid, ferric hydroxide, and chromic acid or manganese sludge (obtained as a by-product from the manufacture of saccharin) (*cf.* Fierz-David, "Künstliche org. Farbstoffe," pp. 321–326, Berlin, 1926).

(6) The general process described under (4) may be modified in various ways, as, for instance, by oxidising a leuco-indamine with a primary aromatic amine.

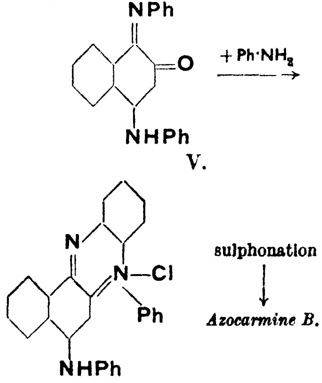
(7) A modern method for the production of certain types of phenyl rosindulines has been devised by Wahl and Lantz (Rev. Gén. Mat. Col. 1923, **28**, 33) and patented by the Société Anon. des Matières Colorantes St. Denis (B.P. 182024, 191064, 206150, 206142, 206488; G.P. 422119):—1-halogeno-2-naphthol (I) is condensed with an aromatic amine to give a 1-arylamino-2-naphthol (II), which may then be oxidised by means of alkali hypochlorite to yield a 1-arylamino-2-naphthaquinone (III).



I. II.

III. IV.

Such quinones readily add on a second molecule of an aromatic amine to give 4-arylamino-1-arylimino-2-naphthaquinones (IV), and these, in turn, will add on a further molecule of an amine to yield a phenylrosinduline. For instance, 4-phenylamino-1-phenylimino-2-naphthaquinone (V) on oxidation in presence of aniline affords a theoretical yield of phenylrosinduline (VI) of sufficient purity for direct sulphonation to *Azocarmine B* ("Colour Index," No. 829) :

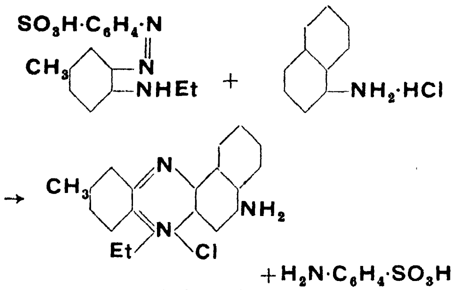


V.

VI.

This direct method of synthesis promises to be of considerable technical value.

(8) The oldest and best known method for the preparation of the safranines on a technical scale consists in heating amino-azo compounds with the hydrochlorides of aromatic amines. Thus the azo dye obtained by coupling diazotised sulphanilic acid with monoethyl-*p*-toluidine, on heating with α-naphthylamine in phenol solution, yields sulphanilic acid and *Induline Scarlet* ("Colour Index," No. 827).



Induline Scarlet.

Again, commercial safranine itself is made by treating a crude mixture of aniline+*ortho*-toluidine with hydrochloric acid and a concentrated solution of sodium nitrite, forming a mixture of aminoazotoluene, aminoazobenzene, aniline, and *ortho*toluidine. Instead, however, of heating the crude mixture directly it is usual to reduce the aminoazo compounds *in situ* with tin or iron, and the resultant mixture of mono- and di-amines is then condensed to a mixture of pheno- and tolusafranines according to method (V).

(9) Certain more complex azonium compounds such as Mauveine may be prepared by the direct oxidation of crude aniline.

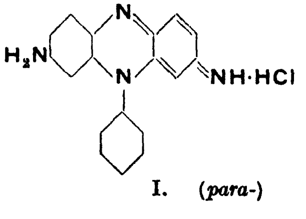
(10) Azine dyes may be prepared by condensing 1-chloro-2 : 4-dinitronaphthalene with *o*-aminodiphenylamine (Kehrmann, Ber. 1923, **56** [B], 2385).

(11) A *summary of methods for preparing azine dyestuffs* is given by Lantz in Ann. Chim. 1934 [xi], **2**, 55, 101.

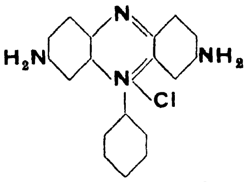
(12) The production of triphenazine-oxazine dyes is described by Kehrmann and Schiedler (Helv. Chim. Acta, 1925, **8**, 1, 9).

(iv) The Structure of Azonium Dyestuffs (*contd.*).—As already pointed out on p. 571, there are several possibilities regarding the structure of these colouring matters and it cannot be said with certainty that the question of *para*- versus *ortho*-quinonoid structure is finally settled, as there is little doubt that in certain cases, at least, the substances may be tautomeric.

Of the two alternative quinonoid formulæ, I and II, for Safranine B,

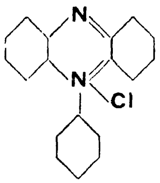


I. (*para*-)



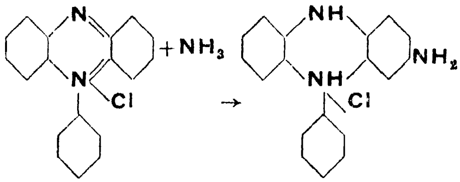
II. (*ortho*-)

a decision could be arrived at by a consideration of the behaviour of the dye with nitrous acid, since I contains only one amino group, whereas II contains two. Actually, one amino group may be readily removed by diazotisation in the ordinary way, yielding *aposafranine*, whilst the second group is considerably more resistant. Kehrmann, however (Ber. 1896, **29**, 2316), by diazotising a sulphuric acid solution of aposafranine, succeeded in removing the second amino group, thus obtaining phenyl-diphenazonium chloride,



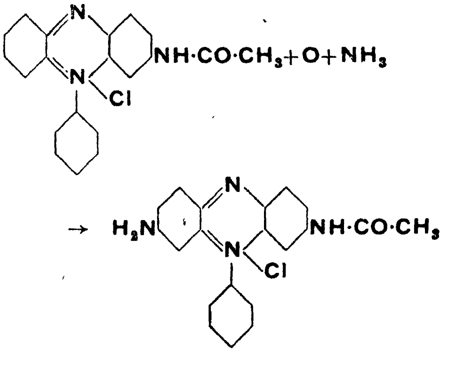
which cannot have a *para*-quinonoid structure.

Kehrmann further showed (Ber. 1897, **30**, 1565, 2620 ; 1900, **33**, 395) that on treating phenyl-diphenazonium chloride with ammonia an amino group is added on (*cf.* p. 571) (just as quinone, for example, adds on hydrochloric acid), yielding leuco-aposafranine :



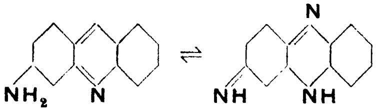
Leuco-aposafranine.

which oxidises at once in air to aposafranine itself. If the latter be then acetylated and again treated with ammonia a further amino group is introduced yielding acetylphenosafranine :



Such a synthesis is readily explicable on the *ortho*-quinonoïd hypothesis, but not with a *para*-quinonoid structure.

We may therefore take it that the behaviour of the azonium group of dyes can be best explained by the assumption of an *ortho*-quinonoid structure, though the possibility of tautomeric change to a *para* form should not be overlooked. It is evident that we are dealing here with an interannular tautomeric system :



and, as is well known, any attempt to determine structure in such cases is very difficult, *e.g.* benzene.

Kehrmann, Havas, and Grandmougin and their pupils have carried out numerous investigations on the structure of azonium dyes. In particular, they have examined the behaviour of some phenazonium compounds with varying concentrations of sulphuric acid. As has already been pointed out, by increasing the concentration of the acid striking colour changes are produced, and the results show that (with few exceptions) the number of colour changes produced increases with the number of amino groups present in the molecule, which is explained by assuming that salt formation takes place progressively, each transformation of a basic group into a salt group causing a colour change.

Frequently the second salt of a diamino compound exhibits colour and spectral relationships identical with those shown by the salt of the monoamino compound, the effect of the acid apparently being to neutralise the chromophoric effects of the particular amino group, *e.g.* the "second" coloration of 1 : 3, 3 : 7, or 3 : 11 diaminophenylphenazonium salts is the same as the "first" coloration of the 3-amino compound (Ber. 1913, **46**, 2802). Where this rule does not hold good the assumption is made that a change has occurred from *ortho*- to *para*-quinonoid structure, or *vice versa*.

The assumption of a change from *ortho*- to *para*-quinonoid rests on some experimental basis : Grandmougin and Smirous (Ber. 1913, **46**, 3425) considered the green tri-acid safranine salts obtained on solution in sulphuric acid to be mixtures of a yellow *ortho*-quinonoid compound and a blue *para*-quinonoid compound, and such green solutions on treatment with sodium nitrite undergo at first only partial diazotisation, but on standing for some days the *para* form slowly rearranges into the *ortho* form and is bis-diazotised, so that on pouring into alcohol phenylphenazine is formed.

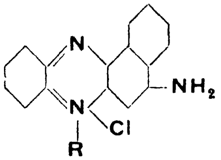
Balls, Hewitt and Newman (J.C.S. 1912, **101**, 1840) from an examination of the absorption curves of various azine dyes considered that these indicated tautomeric change of the safranines, from *ortho*- to *para*-quinonoid according to conditions.

It is not necessary to detail all the various azonium dyes which have been prepared and sold from time to time, as these are fully dealt with in the "Colour Index" (Bradford, 1924), Nos. 827 to 858. The following typical examples may, however, be noted :

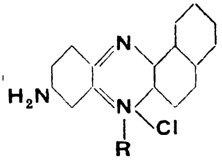
II. (*b*) MONOAMINO DERIVATIVES OF AZONIUM BASES.

(i) **Aposafranine** (phenyl-aminodiphenazonium chloride) is a red dyestuff of no practical importance but of interest as being the prototype of the induline group.

The distinction was formerly made in the case of the aminonaphthaphenazonium derivatives as *Rosindulines* or iso-*Rosindulines*, according to whether the amino group was in the naphthalene nucleus or not :



Rosinduline.

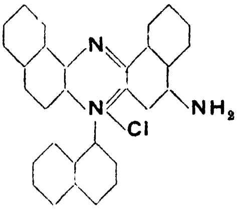


iso-Rosinduline.

This distinction is not now so generally observed (*cf.*, however, "Colour Index").

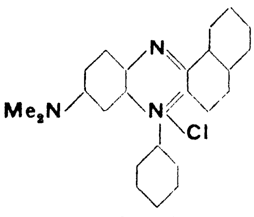
(ii) **Induline Scarlet** ("Colour Index," No. 827) (*see* page 574) (amino-ethyl-tolunaphthazonium chloride), a brilliant red dyestuff. This is now used as a catalyst in discharge printing (*cf.* G.P. 184381). "Rongalite special" (I.G.) and "Hydrosulphite conc. special" (I.G.) both contain this dyestuff.

(iii) **Naphthalene Pink**, *Magdala Red* ("Colour Index," No. 857), from α-aminoazonaphthalene hydrochloride and α-naphthylamine :



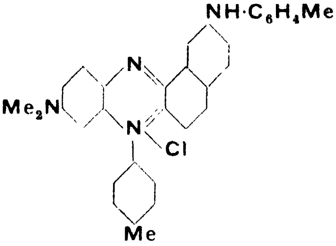
It is accompanied by the corresponding diamino compound and is used to a slight extent for pink shades on silk.

(iv) **Neutral Blue** ("Colour Index," No. 832), from nitrosodimethylaniline hydrochloride and β-naphthylphenylamine (Witt, Ber. 1888, **21**, 719).



It dyes tannin-mordanted cotton in rather dull blue shades of poor fastness.

(v) **Basle Blue** ("Colour Index," No. 836). *p*-Tolyl-dimethylaminopheno-*p*-tolylaminonaphthaphenzonium chloride:



prepared from *p*-nitrosodimethylaniline and 2 : 7-di-*p*-tolyl-naphthylenediamine, dyes wool a reddish-blue and is used for topping indigo.

(vi) **Azine Green GB** ("Colour Index," No. 834) (for formula, *see* p. 573), dyes bluish-green shades and is used to some extent in calico-printing.

II. (*c*) Diamino Derivatives of Azonium Bases.

This includes the groups of phenosafranines, tolusafranines, and naphthosafranines, and includes the technically more important members of the azine group of dyestuffs (p. 573). The methods of production have been already discussed, and it is not therefore necessary to enter into great detail here, but the following typical examples may be mentioned.

Phenosafranine, $C_{18}H_{15}N_4Cl$ ("Colour Index," No. 840), was first prepared by Witt and exhibited in Paris in 1878; it was investigated by Witt and by Nietzki (Ber. 1883, **16**, 466, 871). Phenosafranine is prepared by the joint oxidation of *para*-phenylenediamine and aniline, the mechanism of the process having already been explained (p. 573). A hot dilute aqueous solution of the hydrochlorides of the bases is used, and the oxidation effected by adding sodium or potassium bichromate (or manganese dioxide). The blue colour of the indamine which appears at first is immediately replaced by the red colour of the safranine formed, soda or chalk is added, the solution filtered and the safranine precipitated as the *hydrochloride* by the addition of salt and hydrochloric acid. A yield of 70% of pure dye may be attained by careful working. The hydrochloride forms magnificent green needles, the *sulphate* blue needles. A *diacetyl* derivative is formed on boiling the dyestuff with acetic anhydride and dry sodium acetate.

Phenosafranine has absorption bands at λ 5224 and 5040A° and dyes wool, silk, and tannin-mordanted cotton a brilliant pink. The aqueous solutions are non-fluorescent, but in alcoholic solution a marked greenish-yellow fluorescence is shown.

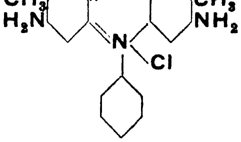
Phenosafranine (or its homologues) may be diazotised and coupled with β-naphthol to yield beautiful basic blue dyes known under various trade names as *Indoine Blue*, *Janus Blue G* (*cf.* p. 570), *Naphthindone BB*, etc. ("Colour Index," No. 135), which are used for dyeing tannin-mordanted cotton and for calico-printing.

Phenosafranine itself has been replaced for dyeing purposes by its homologue, Safranine T, but has recently come again into prominence as a photographic desensitiser, thus enabling panchromatic photographic plates to be safely developed in diffused light (*see* Photography).

The *N*-dimethyl derivative (prepared by the joint oxidation of one molecular proportion each of *p*-phenylenediamine, aniline, and dimethylaniline) has been made under the name of *Fuchsia* or *Methylene Violet BN* ("Colour Index," No. 842) and affords reddish-violet shades; the corresponding diethyl derivative has similar characteristics.

The *tetramethyl-* and *tetraethyl-safranines* from dimethyl- or diethyl-aniline and aniline, discovered by Nietzki, have been sold as *Amethyst Violet* or *Iris Violet* ("Colour Index," No. 847) and dye mordanted cotton brilliant violet shades with a fine crimson fluorescence; their fastness is poor, however. Amethyst violet like safranine has a desensitising action upon photographic plates.

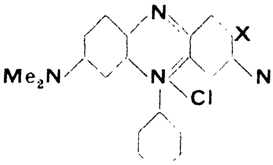
Safranine T is, however, of greater importance and the safranine of commerce consists of a mixture of the isomers of the formula $C_{21}H_{21}N_4Cl$ ("Colour Index," No. 841). It is prepared technically from a mixture of aniline, o-toluidine, and *p*-tolylenediamine: a mixture of aniline and *o*-toluidine is diazotised with hydrochloric acid and a concentrated solution of sodium nitrite to form a mixture of aminoazo compounds, which are reduced with tin or iron to the corresponding mono- and di-amines; these are then oxidised by chromic acid or Weldon mud to a mixture of tolusafranines, of which the symmetrical isomer is Safranine T.



Safranine T.

Safranine T dyes tannin-mordanted cotton in brilliant red shades, which are fast to washing and rather faster to light than the dyeings from safranine itself. Its use is now, however, somewhat restricted owing to the competition of primuline and azo dyestuffs. Of other basic dyes of the safranine series the following may be noted:

Methylene Violet BN ("Colour Index," No. 842), from *asym*-dimethyl-*p*-phenylenediamine and aniline :

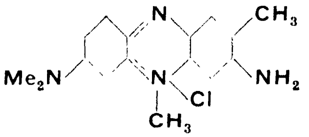


The corresponding homologue (X CH_3) is known as *Clematine* or *Brilliant Heliotrope 2R conc.* ("Colour Index," No. 843).

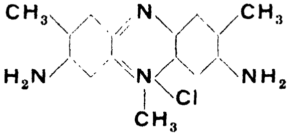
Magdala Red ("Colour Index," No. 857) has already been mentioned on p. 575, amongst the monoamino derivatives, but the commercial dye also contains a considerable proportion of the diamino compound.

Giroflé or Tannin Heliotrope ("Colour Index," No. 852) from *p*-nitrosodimethylaniline hydrochloride and the mixed hydrochlorides of *m*- and *p*-xylidines, is a reddish-violet dye of moderate fastness, but is now mainly of historical interest.

Azine Scarlet ("Colour Index," No. 838), from amino-azotoluene hydrochloride and *o*-amino-dimethyl-*p*-toluidine, was formerly believed to have formula I, but has since been shown by Cohen and Crabtree (J.C.S. 1921, **119,** 2055) to possess formula II. The dyestuff I has been prepared and is a magenta-coloured dye :



I.



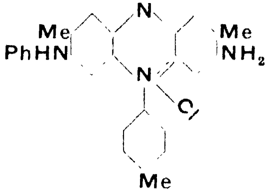
II.

Mauveine, $C_{27}H_{25}N_4Cl$ ("Colour Index," No. 846) is of great historical interest, since its discovery and commercial application was the starting point for the development of the whole "aniline dye" industry. It was prepared in 1857 by the late Sir W. H. Perkin, while a student of Prof. A. W. Hofmann, by oxidising a solution of the sulphate of crude aniline by means of potassium dichromate, and extracting the black insoluble product obtained, with alcohol (Perkin, B.P. 1984 of 1856 ; J.C.S. 1862, **14,** 232 ; Proc. Roy. Soc. 1863, **12,** 713, etc. For detailed references consult "Colour Index," No. 846). The dye was formerly sold as a violet paste and when first prepared was in great demand and very costly. It is insoluble in cold water, sparingly soluble in hot water, readily so in spirit. In strong sulphuric acid it forms an olive-green solution, changing on dilution through green and blue to purple.

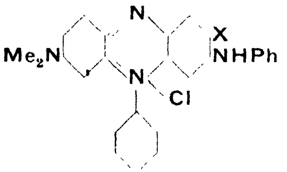
It was known under a variety of names, such as "Mauve," "Perkin's Purple," Rosolane, Aniline Violet, Tyrian Purple, etc., and was used mainly for dyeing silks in mauve shades, which at the time of its discovery were so widely used that "Punch" referred to it as an outbreak of "Mauve Measles"!

It was used for many years for the Victorian violet penny stamps, but is now practically obsolete.

Its structure remained long unknown, but it is now recognised as phenylated tolusafranine of the structure (chloride) :



Closely related to Mauveine is the indigo-blue dye *Indazine,* $C_{26}N_{23}N_4Cl$ ("Colour Index," No. 849), obtained by heating *sym*-diphenyl-*m*-phenylenediamine with *p*-nitrosodimethylaniline hydrochloride. It has the structure :

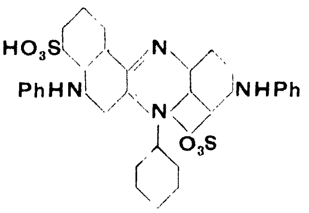


but may also contain a substance with the hydrogen X of above formula substituted by

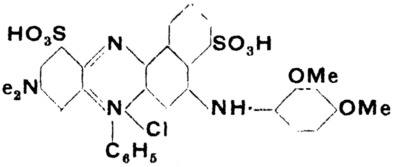
$$—NH·C_6H_4·NMe_2$$

It is a dye having good fastness to washing, alkalis and acids, and fairly fast to light.

Dyes of greater practical importance to-day are the *Wool Fast Blues* ("Colour Index," No. 833) and the *Indocyanines, e.g.*



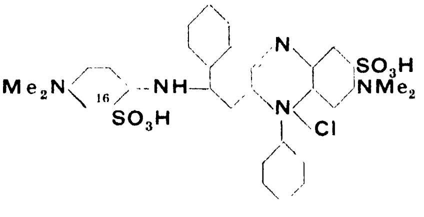
Wool Fast Blue BL.



Indocyanine 6B (?).

A blue dyestuff of the Indocyanine type (*cf.* above formula) may be obtained by oxidising together (1 : 3-dialkoxyanilino)-naphthalene-8-sulphonic acid with *p*-aminodiphenylamine sulphonic acid (I.G. Farbenind. A.-G., G.P. 186597, 186598, 193472 ; B.P. 275301, 275724 ; Fierz-David, J. Soc. Dyers & Col. 1929, **45**, 138).

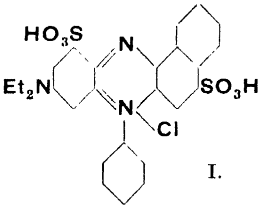
The Novazol Acid Blues and Polar Blues (Geigy & Co.) of the type :



are modern types of azonium dyestuffs of considerable fastness to light, alkalis, etc., and with good levelling properties.

Such blue and bluish-green azine dyes may be obtained by condensing a di- or tri-sulphonated *iso*rosinduline with a sulphonated *p*-aminodialkylarylamine, or with *p*-aminophenol; for example, diethyl*iso*rosinduline disulphonic acid may be condensed with 6-ethylamino-*m*-toluidine-4-sulphonic acid. It is suggested that the presence of the sulphonic group in position "16" is partly responsible for the increased fastness of the products (Geigy & Co., B.P. 265986, 282803, 284614, 284615, 285486, 297441, 300549 ; Swiss P. 124764 ; G.P. 553942, 504331).

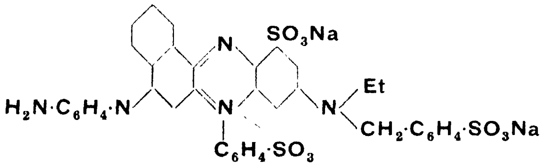
In G.P. 465581, U.S.P. 1683559, Geigy & Co. prepare blue acid dyes of the same type by treating 11-chloro-diethyl*iso*rosinduline with sodium bisulphite, to yield *iso*rosinduline-5 : 11-disulphonic acid I (the chlorine being replaced by a sulphonic group),



I.

which is then further condensed with *p*-phenylenediamine sulphonic acid, or 5-amino-*o*-cresol-4-sulphonic acid, etc.

Pure blue wool dyes of the analogous type :



are described in B.P. 221975 (A.-G. für Anilin-Fabr.).

III. Miscellaneous.

The following more recent technical developments in the field of azine and azonium dyestuffs may be noted.

Safranine sulphonic acids are obtained by oxidising alkylbenzylaniline sulphonic acids together with derivatives of diphenylamine sulphonic acids to the corresponding indamine and then continuing the process in presence of an aromatic amine (A.-G. für Anilin-Fabr., F.P. 417669).

A safranine disulphonic acid is obtained by the joint oxidation of *p*-iminodiphenylamine sulphonic acids of tertiary amines, in which the *para* position is free, such as an alkylbenzyl sulphonic acid (Farbw. Hoechst., G.P. 243491 ; F.P. 426790).

Yellowish-red safranine dyes result from the condensation of nitrosomethyl-*o*-toluidine and *m*-aminomethyl-*p*-toluidine ; or by oxidising together a mixture of methyl-*p*-tolylenediamine and methyl-*m*-tolylenediamine (Durand, Huguenin & Co., B.P. 2933 of 1915 ; G.P. 282346, 287271).

Safranine dyes may be converted into the corresponding gallocarboxylic acid salts (F. Bayer & Co., G.P. 285500).

By the phosgenation of sulphonated azine dyes products are obtained which dye level shades on viscose (Adams, Green, Saunders and Brit. Dyestuffs Corp., Ltd., B.P. 296803). The same inventors also claim the production of azine dyes by the use of hydroxyalkylamines of the type $RR'{\cdot}N{\cdot}C_6H_4{\cdot}OH$; thus a basic violet dye is obtained from nitrosodimethylaniline with *sym*-dihydroxyethyl-*m*-phenylenediamine (B.P. 182031). This dyestuff may be converted into the acid sulphuric ester which dyes wool in reddish-blue shades (B.P. 181750).

The conversion of naphthaphenazine and dinaphthazine sulphonic acids into the corresponding hydroxy compounds, by heating with 10% aqueous caustic alkali is claimed by I.G. Farbenind. A.-G. in B.P. 322209, the same firm also describe the diarylation of leuco-phenosafranines at 180°–260° and subsequent oxidation to sky-blue basic dyes (B.P. 359398).

Yellow to brown hydroxy- and amino-phenanthranaphthazines have been prepared from phenanthraquinone and 1 : 2-naphthylenediamines or their 5-sulphonic acids by Sircar and Dutt, who have also obtained naphthaflavindulines which dye wool in red to blue shades (J.C.S. 1922, **121**, 1944, 1952).

In B.P. 335896 the Soc. Chem. Ind. in Basle obtain dyes by coupling hydroxysulphonaphthaphenazines with suitable diazo-components and the fabrics dyed with these substances may be chromed, coppered, etc.

The use of 4-amino-2′-methoxy-5-methyl-diphenylamine-2-sulphonic acid as an intermediate for the production of safranines is claimed by Du Pont de Nemours and Co., in U.S.P. 1934727. Greenish-blue azine dyes may be obtained from 1 : 3-diarylaminonaphthalene-8-sulphonic acid and 4 : 4′-diaminodiphenylamine sulphonic acid (I.G. Farbenind. A.-G., B.P. 414138), whilst the production of blue and violet azine dyestuffs containing the radical $\mathbf{—NR{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H}$ is claimed by the same firm in B.P. 417388.

By oxidising 2 : 3-aminonaphthol and its derivatives (in which the hydroxy groups are protected by acylation or alkylation) dihydroxynaphthazines are obtained, which may be coupled with diazo components in substance or on the fibre (I.G. Farbenind. A.-G., B.P. 421611). The production of further types of azine dyes is claimed by the same firm in B.P. 300178 and 328291.

Analytical Methods.—For the determination of safranine (as picrate) Castiglione recommends titration of an aqueous solution of the dye with 0·01*N*-picric acid, in presence of chloroform, until the aqueous solution is colourless, as safranine picrate is insoluble in water but readily soluble in chloroform (Z. anal. Chem. 1934, **97**, 334).

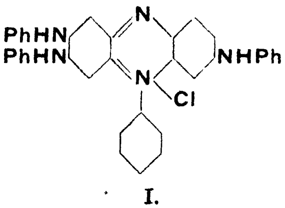
For examining the structure of azine dyestuffs Bass recommends hydrolysis by heating the dye under pressure with a solution of hydrochloric acid in glacial acetic acid, and examining the absorption spectra of the hydroxy products thus obtained, since the classical methods of reduction, oxidation, etc., do not, in general, give identifiable products (Helv. Chim. Acta, 1933, **16**, 403).

The application of safranines and *apo*safranines in oxidation-reduction systems has been examined by Chen, Clark and Stichler (J. Amer. Chem. Soc. 1933, **55**, 891, 4097).

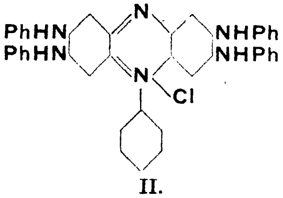
The reduction of hydroxyphenazine and rosinduline in stages, in acid solution, has been dealt with by Michaelis (J. Biol. Chem. 1931, **92**, 211).

The therapeutic use of mercurated safranines has been claimed by the Saccharin Fabrik vorm. Fahlberg, List & Co. (G.P. 286907), whilst the product obtained by combining safranine with tannin has been recommended as a drug for the treatment of trypanosoma and other protozoal infections.

IV. Indulines.—The indulines obtained by prolonged heating of aminoazo-benzene, aniline, and their salts are regarded as being composed mainly of higher phenylated derivatives of phenosafranine, such as *anilino-diphenylphenosafranine* I, and *di-anilino-diphenylsafranine*, etc., II :



I.



II.

and are thus related to the safranines. For convenience they are discussed in a separate article (*v.* INDULINES).

V. Nigrosines.—These are presumably still more complex azine derivatives related to the safranines (*v.* NIGROSINES).

Aniline Black (*v.* DYEING) is also closely related to the azine group.

VI. Literature.—For further references, *see* " Colour Index " (Bradford, 1924), Nos. 824 to 858 ; " Lehrbuch der organischen Chemie," Meyer and Jacobson (Berlin, 1920), vol. 2 (iii), pp. 1345–1454 ; " Künstliche organische Farbstoffe," H. E. Fierz-David (Berlin, 1926), pp. 304–350, and " Ergänzungsband " (Berlin, 1935, pp. 19–23) ; "The Synthetic Dyestuffs," Thorpe and Linstead, Griffin, 1933 ; " Textbook of Dye Chemistry," Georgievics-Grandmougin, translated and revised by F. A. Mason (London, 1920), pp. 340–367 ; Friedländer's "Fortschritte in der Teerfarbenfabrikation." F. A. M.

AZOBENZENE, $C_6H_5{\cdot}N : N{\cdot}C_6H_5$, is obtained from nitrobenzene by partial reduction with a variety of agents, of which the most generally employed are iron filings (Gattermann, "Die Praxis des organischen Chemikers," 12th ed., 1914, 213), or iron and caustic soda (Fierz-David, Grundlegende Operationen der Farbenchemie, 3rd ed., 1924, 67), or zinc dust and caustic soda (Alexejeff, Jahresber. 1867, 503). The reduction may also be effected by means of hydrogen in the presence of a catalyst, especially thallium (Henke and Brown, J. physikal. Chem. 1922, **26**, 631), and electrolytically (Elbs and Kopp, J.S.C.I. 1898, **17**, 1137 ; Löb, Ber. 1900, **33**, 2329). Azobenzene is also formed by the oxidation of hydrazobenzene (Gattermann, *ibid.*, 22nd ed., 1930, 178) or of phenylhydrazine with bleaching powder (Brunner and Pelet, Ber. 1897, **30**, 284).

Azobenzene forms orange-red crystals, m.p. 68°, b.p. 295°. It is readily soluble in alcohol and ether, but insoluble in water. It is reduced by weak agents to hydrazobenzene (Alexejeff, Annalen, 1881, **207**, 327 ; Walther, J. pr. Chem. 1896 [ii], **53**, 433) and by stronger agents or electrolytically to benzidine (Bordenstein, G.P 172569 ; Schultz, Ber. 1884, **17**, 464 ; Mentha and Heumann, Ber. 1886, **19**, 2970 ; Löb, Ber. 1900, **33**, 2329). It reacts with benzene in the presence of hydrogen chloride and aluminium chloride to give intermediate products convertible into aminodiphenyl (Pummerer, Ber. 1885, **18**, 1481). With ammonium hydrogen sulphite it forms benzidinesulphamic acid (Spiegel, Ber. 1885, **18**, 1481), and with *p*-phenylenediamine a soluble induline dye (G.P. 53198). Concentrated sulphuric acid dissolves azobenzene without alteration, but the fuming acid at 130° converts it into azobenzene-4-sulphonic acid, m.p. 127° (Griess, Annalen, 1870, **154**, 208; Janovsky, Monatsh. 1881, **2**, 219). Nitration yields 4-nitroazobenzene, m.p. 149°, and 4:4′-dinitroazobenzene, m.p. 221° (Gerhardt and Laurent, Annalen, 1850, **75**, 73), and bromination gives 4-bromoazobenzene, m.p. 94°, and 4:4′-dibromoazobenzene, m.p. 205° (Werigo, Annalen, 1865, **135**, 178; 1873, **165**, 199). These and many other substitution derivatives of azobenzene and methylazobenzenes have been investigated by Burns, McCombie, and Scarborough (J.C.S. 1928, 2928).

AZOBENZENE RED *v.* DYESTUFFS, AZO.

AZOCARMINE B *v.* AZINES.

AZODERMIN, 4-acetaminoazotoluene, is used as a wound dressing.

AZO-DYES *v.* DYESTUFFS, AZO.

AZO-ACID YELLOW, -ALIZARIN YELLOW, -BLACK or NAPHTHOL BLACK, -BLUE, -BORDEAUX, -CHROMINE, -COCCINE, -COCHINEAL, -CORALLINE, -COREOSINE, -FLAVINE, -FUCHSINES, -VIOLET *v.* DYESTUFFS, AZO.

AZOFLAVIN, AZOGEN RED, AZO-GRENADINES *v.* DYESTUFFS, AZO.

AZOIMIDE (Hydrazoic Acid), HN_3, was isolated by T. Curtius in 1890 (Ber. 1890, **23**, 3023) from benzoyl azide. This compound, obtained by him by the action of nitrous acid (sodium nitrite+acetic acid) on benzoyl hydrazine:

$$C_6H_5\cdot CO\cdot NH\cdot NH_2 + HO\cdot NO \rightarrow C_6H_5\cdot CO\cdot N(NO)\cdot NH_2 \rightarrow C_6H_5\cdot CO\cdot N_3,$$

was hydrolysed by digestion with absolute alcoholic sodium ethoxide, whereby sodium azide was formed, and could be thrown out of solution by the addition of ether:

$$C_6H_5\cdot CO\cdot N_3 + NaOEt = C_6H_5\cdot CO_2Et + NaN_3$$

Similarly hippuryl hydrazine forms hippurazide with nitrous acid, hydrolysis with ammonia then yielding ammonium azide (Curtius, Ber. 1891, **24**, 3341):

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2 \xrightarrow{HO\cdot NO} C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_3 \xrightarrow{NH_4OH} C_6H_5\cdot CO\cdot NH\cdot CONH_2 + NH_4\cdot N_3$$

In general, methods for the preparation of azoimide and its derivations proceed by way of the alkali metal salts.

Formation of Hydrazoic Acid and the Azides.—(1) A most convenient method for the preparation of sodium azide, due to Wislicenus (Ber. 1892, **25**, 2084), is by the action of nitrous oxide at 200°–250° upon sodamide, which is readily made by the action of dry ammonia upon metallic sodium:

$$NaNH_2 + ON_2 = NaN_3 + H_2O$$

(2) By the action of saturated aqueous silver nitrite upon hydrazine sulphate, crystalline silver azide is deposited (Angeli, Ber. 1893, **26**, 885).

(3) The action of ethereal ethyl nitrite upon a mixture of hydrazine hydrate and sodium methoxide gives a nearly quantitative yield of sodium azide. The free acid may be similarly prepared in over 80% yield by shaking hydrazine sulphate with sodium hydroxide and ethyl nitrite (Thiele, Ber. 1908, **41**, 2681).

(4) 2:4-Dinitrobenzazide, prepared from 2:4-dinitroaniline, yields potassium azide on hydrolysis with alcoholic potash (Nölting and Grandmougin, Ber. 1891, **24**, 2546); see also Nölting, Grandmougin and Michel, Ber. 1892, **25**, 3328:

$$\begin{tikzcd}
& C_6H_3(NO_2)_2\cdot NH_2\cdot HNO_3 \arrow[d, "HNO_2"] \\
& C_6H_3(NO_2)_2\cdot N_2\cdot NO_3 \arrow[d, "Br"] \\
& C_6H_3(NO_2)_2\cdot NBr\cdot NBr_2 \arrow[d, "NH_3"] \\
C_6H_3(NO_2)_2OK + KN_3 & C_6H_3(NO_2)_2\cdot N_3 \arrow[l, "KOH"']
\end{tikzcd}$$

(5) Free azoimide is formed by the action of aqueous hydrazine on a benzene solution of nitrogen trichloride (Tanatar, Ber. 1899, **32**, 1399).

$$N_2H_4 + NCl_3 = 3HCl + HN_3$$

(6) Potassium nitrite decomposes hydrazine sulphate (Dennstedt, Chem.-Ztg. 1897, **21**, 876).

$$N_2H_4\cdot H_2SO_4 + KNO_2 = KHSO_4 + N_3H + 2H_2O$$

The free acid may be prepared in quantity by heating the sodium salt with dilute sulphuric acid, when the volatile hydrazoic acid distils over. The following method of Wöhler and Martin (Ber. 1917, **50**, 586) is safer and more convenient:—5 g. of powdered sodium azide are added to 100 c.c. of ether containing 2 c.c. of sulphuric acid, sodium sulphate is removed by filtration, leaving an ethereal solution of free azoimide.

Anhydrous azoimide is a colourless, mobile liquid boiling at 37°C., and is readily soluble in water. The heat of formation is:

$$3N + H + aq. = HN_3aq. - 61{,}000 \text{ g.-cal.}$$

(Berthelot and Matignon, Compt. rend. 1891, **113**, 672). It has an unpleasant odour, and is very poisonous. The vapour rapidly attacks the mucous membrane, while the aqueous acid blisters the skin. The free acid is, moreover, highly explosive and extremely sensitive to shock. The salts, which crystallise in the anhydrous state, are also highly explosive, with the exception of the relatively stable alkali and alkaline earth azides. Thermal decomposition of the latter affords a convenient mode of preparing the pure free metal, which has found commercial application, *e.g.* $BaN_6 = Ba + 3N_2$. For the properties of the metallic azides, *see* AZIDES.

Hydrazoic acid is a weak acid, comparable in strength with acetic acid (West, J.C.S. 1900, **77**, 705), and generally resembles the halogen acids in properties, giving insoluble silver, lead, mercurous and thallous salts. The analogy with the "pseudohalogen" thiocyanic acid is especially close, azides giving an intense red colour with ferric chloride, while the N'_3 ion, like CNS', readily enters the complex in cobaltammines (Strecker and Oxenius, Z. anorg. Chem. 1934, **218**, 151). In dilute (7%) solution hydrazoic acid dissolves zinc and magnesium with evolution of hydrogen. Reduction of the azoimide takes place, however, with sodium amalgam or zinc and acid, hydrazine and ammonia being formed ; reduction with sodium sulphide or ferrous hydroxide forms little hydrazine. Salts of heavy metals yield only basic azides, while on boiling ferric, chromic, aluminium or thallium salts with the free acid, the corresponding hydroxides are precipitated quantitatively.

Azides may be determined volumetrically by direct titration with silver nitrate, using potassium chromate as indicator (C. Majrich, Chem. Obzor. 1930, **5**, 3 ; A. 1931, 186), or by means of the reaction with nitrous acid :

$$HNO_2+HN_3=H_2O+N_2O+N_2$$

the acidified solution of the azide being titrated with sodium nitrite, using ferric chloride as indicator (Reith, Pharm. Weekblad, 1930, **67**, 475). Nitrites may be similarly determined, an excess of azide being used and subsequently titrated back with iodine and thiosulphate. (*See also* Feigl and Chargoff, Z. anal. Chem. 1928, **74**, 376 ; Martin, J. Amer. Chem. Soc. 1927, **49**, 2133.)

Chloroazide, N_3Cl, is obtained by the action of sodium hypochlorite on sodium azide ; it is a colourless gas, the thermal decomposition of which is accompanied by a chemiluminescence (Raschig, Ber. 1908, **41**, 4194).

Bromazide, N_3Br, is formed by the action of bromine vapour, diluted with nitrogen, upon silver azide (D. A. Spencer, J.C.S. 1925, **127**, 216). It is an orange liquid, melting at −45° and is highly explosive.

Iodazide, N_3I, is an unstable, nearly colourless substance, formed by shaking a suspension of silver azide with a solution of iodine in ether at 0° (Hantzsch, Ber. 1900, **33**, 522); alkalis convert it into the corresponding alkali azide:

$$N_3I+2KOH=KN_3+H_2O+KIO,$$

a similar hydrolysis slowly taking place with water alone: $N_3I+H_2O=HN_3+HIO$.

Ammonium azide, N_4H_4, and *hydrazine azide*, N_5H_5, obtained by the action of lead azide on ammonium and hydrazine sulphate respectively, are readily volatile and explosive.

Potassium azide reacts with carbon disulphide, forming *potassium azidothiocarbonate*,

$$KS{\cdot}CS{\cdot}N_3,$$

(Browne and Hoel, J. Amer. Chem. Soc. 1932, **44**, 2106), which on electrolysis or very mild oxidation gives the unstable azidocarbondisulphide $N_3{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}N_3$, a "pseudohalogen." This reacts with alkalis similarly to chlorine:

$$(SCSN_3)_2+2KOH$$
$$=KS{\cdot}CS{\cdot}N_3+KOS{\cdot}CS{\cdot}N_3+H_2O,$$

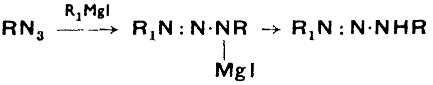
or, on heating,

$$3KOS{\cdot}CS{\cdot}N_3=2KS{\cdot}CS{\cdot}N_3+KO_3S{\cdot}CS{\cdot}N_3$$

(Browne, Hoel, Smith and Swezey, J. Amer. Chem. Soc. 1923, **45**, 2541).

Tetramethylammonium azide, NMe_4N_3, formed by the action of tetramethylammonium iodide on silver azide, is amongst the most stable salts. It forms tetragonal crystals ($a : c = 1 : 0{\cdot}7245$) which may be ground up or rapidly heated without explosion, but begin to decompose about 125°C. (Friedlander, J. Amer. Chem. Soc. 1918, **40**, 1945).

Methyl azide, CH_3N_3, is formed by the action of dimethyl sulphate on sodium azide (Dimroth and Wislicenus, Ber. 1905, **38**, 1573). With magnesium methyl iodide, it is converted into dimethyltriazene—a general reaction (Dimroth, Ber. 1906, **39**, 3905) :



$$RN_3 \xrightarrow{R_1MgI} R_1N:N{\cdot}\underset{\displaystyle MgI}{\underset{|}{N}}R \rightarrow R_1N:N{\cdot}NHR$$

Phenyl azide (diazobenzeneimide), $C_6H_5N_3$, was the earliest known compound of azoimide, having been prepared by Griess (Annalen, 1866, **137**, 65, 77) by the action of ammonia on diazobenzene perbromide:

$$C_6H_5{\cdot}NBr{\cdot}NBr_2+4NH_3=C_6H_5{\cdot}N_3+3NH_4Br$$

It is a pale yellow oil, volatile in steam. Other methods for the preparation of aryl azides are:

(2) the decomposition of the diazonium sulphate with hydroxylamine:

$$RN_2{\cdot}HSO_4+NH_2{\cdot}OH=H_2SO_4+H_2O+RN_3$$

(3) the action of nitrous acid on the arylhydrazine:

$$RNH{\cdot}NH_2 \xrightarrow{HNO_2} RN(NO){\cdot}NH_2$$
$$\rightarrow RN_3+H_2O$$

(4) the decomposition of the β-arylsemicarbazides with sodium hypochlorite:

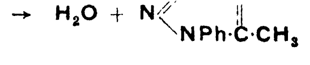
$$RNH{\cdot}NH{\cdot}CONH_2 \rightarrow RN:N{\cdot}CO{\cdot}NH_2$$
$$\rightarrow RN:N{\cdot}NH_2 \rightarrow RN_3$$

(5) the reaction of the diazonium salt with chloroamine:

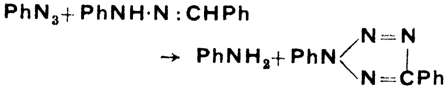
$$RN_2Cl+NH_2Cl \rightarrow RN:N{\cdot}NHCl,HCl$$
$$\rightarrow RN_3+HCl$$

The aryl azides are decomposed on heating with acids; thus phenyl azide with hydrochloric acid yields *o*- and *p*-chloroaniline, nitrogen being evolved ; with sulphuric acid, aminophenols are formed. With hot alcoholic potash, *o*- and *p*-nitrophenyl azides are converted into azoimide and the corresponding nitrophenol.

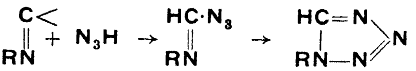
β-Ketonic esters condense with azides, forming triazoles (Ber. 1902, **35**, 4041):



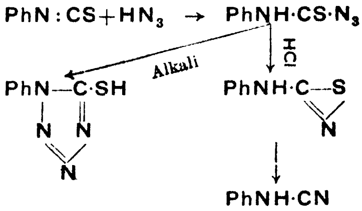
Tetrazoles are similarly formed with benzaldehyde aryl-hydrazones (Ber. 1907, **40**, 2402), *e.g.* :



and with *iso*cyanides (Oliveri-Mandala, Gazzetta, 1918, ii, **48**, 35), *e.g.* :



*iso*Cyanic and *iso*thiocyanic esters yield first the azide of the corresponding carbamic acids, which is converted by alkalis into the isomeric tetrazole derivative, whilst treatment with hydrochloric acid results in the loss of two nitrogen atoms from the molecule, and heating in an indifferent solvent in the elimination of an atom of sulphur, ultimately giving cyanamides (Oliveri-Mandala, Gazzetta, 1921, ii, **51**, 195), *e.g.* :



Tetrazole itself is formed by the addition of azoimide to hydrocyanic acid (*i.e.* potassium azide and cyanide in presence of hydrochloric acid), a method which has been applied to the technical manufacture of tetrazole for explosives (Weil, G.P. 390396).

The *acyl azides* (*e.g.* benzoyl azide, referred to earlier) may undergo decomposition in several ways :

(*a*) In alcohol, urethanes are formed :

$$PhCON_3+EtOH = N_2+NHPh\cdot COOEt$$

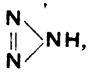
(*b*) On boiling with water, a disubstituted urea is produced :

$$2PhCON_3+H_2O = 2N_2+CO(NHPh)_2+CO_2$$

(*c*) On heating in benzene solution, the product is an *iso*cyanate :

$$PhCO\cdot N_3 = N_2+PhN\cdot CO$$

The structure of the azides has provoked much controversy, Thiele (Ber. 1911, **44**, 2522) having advocated on chemical grounds the replacement of the cyclic structure,



early allotted to azoimide, by a linear formula,

$$HN:N:N$$

The X-ray examination of the crystalline metallic azides, and of cyanuric triazide (Hendricks and Pauling, J. Amer. Chem. Soc. 1925, **47**, 2904 ; Knaggs, Proc. Roy. Soc. 1935, A, **150**, 576) has indicated a straight chain configuration for the $-N_3$ group in these compounds. It has been held, however, that in the case of the organic azides, the physical properties (parachors, boiling-points, dipole moments) agree with the cyclic formula (Lindemann and Thiele, Ber. 1928, **61** [B], 1529 ; Sutton, Nature, 1931, **128**, 639, 872 ; Hantzsch, Ber. 1933, **66** [B], 1349 ; *see*, however, Bergmann and Schütz, Z. physikal. Chem. 1932 [B], **19**, 389). The probable explanation lies in a resonance or rapid alternation between the two linear forms :

$$R\cdot N:N \rightleftharpoons N \rightleftharpoons R\cdot N \leftarrow N:N,$$

a view which explains the dipole moments and agrees best with thermochemical data (Sidgwick, Trans. Faraday Soc. 1934, **30**, 801). J. S. A.

AZOLITMIN *v.* LITMUS.

AZONIUM BASES *v.* AZINES.

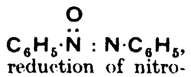
AZOPHOR-BLACK, -BLUE, -RED, -ROSE, AZOPHOSPHINES *v.* DYESTUFFS, Azo.

AZOTE. A name given to nitrogen by Lavoisier, and hence commonly used in French literature to designate that element.

AZOTOMETER. *Nitrometer.* An apparatus for collecting and measuring the nitrogen evolved in the quantitative analysis of certain nitrogen compounds.

AZOXINE COLOURING MATTERS *v.* OXAZINE DYESTUFFS.

AZOXYBENZENE,

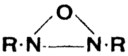


$C_6H_5\cdot\overset{O}{\overset{\cdot\cdot}{N}}:N\cdot C_6H_5$, is prepared by the partial reduction of nitrobenzene by means of sodium in methyl alcohol (Klinger, Ber. 1882, **15**, 866 ; 1883, **16**, 941 ; Moltschanovsky, Ber. 1882, **15**, 1575 ; 1883, **16**, 81) or sodium arsenite (Loesner, B.P. 1555 ; Bigelow and Palmer, Organic Syntheses, 1931, **11**, 16). The reduction may also be effected by sulphides (G.P. 216246, 204653), charcoal and alkali (G.P. 210806), zinc dust and a salt solution (G.P. 43230), lead suboxide (G.P. 486598), iron and alkali (Russ. P. 28218, 29172 ; Chem. Zentr. 1933, II, 3049) or electrolytically (G.P. 127727, 138496 ; Kerns, Trans. Electrochem. Soc. 1932, **62**, 125). Von Auwers (Ber. 1928, **61** [B], 1041) recommends the preparation of azoxybenzene by oxidising azobenzene with hydrogen peroxide.

Azoxybenzene forms pale yellow rhombic needles of m.p. 36° and d_4^{26} 1·1590. According to Knipscheer (Rec. trav. chim. 1903, **22**, 21), it is obtainable also in colourless plates. It is volatile in steam at 140°–150°, insoluble in water but readily soluble in alcohol, ether and light petroleum. It isomerises in sunlight to *o*-hydroxyazobenzene and in conc. sulphuric acid mainly to *p*-hydroxyazobenzene (Wallach, Ber. 1880, **13**, 525 ; 1881, **14**, 2617 ; Bamberger, Ber. 1900, **33**, 3192). When heated with non-volatile substances it decomposes into aniline and azobenzene. Mild reducing agents convert it into hydrazobenzene, stronger agents chiefly to aniline. By heating with conc. nitric acid, two isomeric nitroazoxybenzenes are obtained (Linin, Annalen, 1860, **114**, 217).

Other azoxy-compounds can be obtained by similar methods. Those from *m*-nitraniline, from the nitrotoluidines of m.p. 78° and 107°, and from the nitroxylidine melting at 123° are a source of azo-dyes for cotton and wool (G.P. 44045, 44554).

The symmetrical structure originally assigned to azoxy-compounds

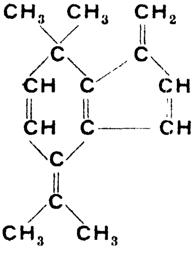


has been abandoned as a consequence of Angeli's observation that two isomeric azoxy-compounds could be obtained from certain unsymmetrical azo-compounds (Atti R. Accad. Lincei, 1911 [v], **20,** 896 ; **20** [ii], 170 ; 1913 [v], **22**, i, 201, 282 ; 1927 [vi], **5**, 819 ; Gazzetta, 1921, **51**, i, 35), his conclusion having since been confirmed by spectroscopic evidence (von Auwers and Heimke, Ber. 1928, **61,** 1037). Azoxybenzene has the stable, *trans* configuration (Gehrckens and Müller, Annalen, 1933, **500,** 296). The labile cis-isomer, iso*azoxybenzene,* m.p. 84°, if rapidly heated, is formed with azoxybenzene by the action of alcoholic caustic soda on nitrobenzene and is separated by taking advantage of its insolubility in light petroleum (Reissert, Ber. 1909, **42,** 1367). It forms nearly colourless needles, which are stable at room temperature but above 67° are gradually converted to normal azoxybenzene.

AZULENE, $C_{15}H_{18}$. An intensely blue liquid hydrocarbon, found in the oils of cubebs, amyris, guaiacum, gurjun, eucalyptus, camomile and milfoil, and in certain brown-coal tars. It has b.p. 295°–300° (167°–168°/12 mm.), d_4^{25} 0·9738. When exposed to light and air, it is converted into a brown resin. It is soluble in sulphuric acid, giving a fluorescent solution, and forming a sulphonic acid yielding a crystalline sodium salt which is soluble in water. It forms a *picrate,* m.p. 120°, and a *styphnate,* m.p. 98°–99°, which are valuable for purposes of identification.

Azulene may be hydrogenated in the presence of palladium black to the compound $C_{15}H_{28}$, b.p. 130°–140°/20 mm., d^{22} 0·8920 (Kremers, J. Amer. Chem. Soc. 1923, **45,** 717), while in the presence of colloidal palladium, Ruhemann and Lewy have obtained the octahydro compound, $C_{15}H_{26}$, b.p. 123°–124·5°/10 mm. (Ber. 1927, **60** [B], 2459). It is unsaturated to bromine and nitrosyl chloride, but no well-defined compounds have been isolated. Sherndal has shown the presence of four double bonds (J. Amer. Chem. Soc. 1915, **37,** 167, 1537). Oxidation with alkaline permanganate solution yields carbon dioxide, acetone, acetic acid, and a homologue of phthalic acid (Kremers).

Ruzicka and Haagen-Smit (Helv. Chim. Acta, 1931, **14,** 1104) have suggested the following structural formula for azulene :



According to Huebner and Graebe (Arch. exp. Path. Pharm. 1933, **22,** 950) the anti-inflammatory action of camomile oil is due to the presence of azulene.

AZULIN *v.* TRIPHENYLMETHANE DYESTUFFS.

AZURE BLUE. Name applied to three different pigments : *Thénard's Blue,* $CoO{\cdot}Al_2O_3$; *cobalt blue,* potassium cobaltous silicate ; *ultramarine,* an aluminium sodium silicate containing sulphur.

AZURE COPPER ORE *v.* AZURITE.

AZURIN, $C_{35}H_{32}N_4O_3$. Obtained by heating salicylic aldehyde, 3 mols., with *o*-tolylenediamine, 2 mols., at 135°. Colourless tables, m.p. 250·5°, giving blue fluorescent solutions (Ladenburg, Ber. 1878, **11,** 596).

AZURITE (*v.* CHESSYLITE). There is considerable confusion between the names azurite, lazurite, and lazulite, which have been indiscriminately applied to various minerals of a blue colour. The adjectives azure and lazure are derived from the Persian lazhward, meaning blue, and applied to lapis-lazuli. The blue copper carbonate was early known as cuprum lazureum, cæruleum montanum, azure copper ore, etc. ; later names applied to this mineral are azurite (F. S. Bendant, 1824), lasur (W. Haidinger, 1845), and lazurite (F. Kobell, 1853). But the name azurite had been earlier (R. Jameson, 1805) applied to the blue phosphate of aluminium, magnesium and iron, now known as lazulite ; and lazurite is now used for the essential constituent (ultramarine) of lapis-lazuli. Azurite is also a current trade name for a blue-black ink. The name chessylite (W. H. Miller, 1852) has not been applied to any other mineral but the blue copper carbonate, and it is free from any ambiguity. L. J. S.

B

B-ACID. 1-Amino-8-naphthol-3-5-disulphonic acid. Intermediate product for the manufacture of dyes.

B.R.I. *v.* ARSENICALS, ORGANIC.

B_1 VITAMIN. BERI-BERI, a disease still widely prevalent in the East, and attributable to deficiency of vitamin B_1, is caused by the consumption of a one-sided dietary, most usually consisting largely of polished rice. As met with in humans the disease is no doubt often complicated by concurrent deficiencies of other factors, for obviously the natural diet of man but rarely approximates to that which can be used artificially in the laboratory for the production of experimental beri-beri in animals—when conditions can be so arranged that all other known dietary factors are provided in abundance. Nevertheless, the belief that the syndrome as commonly met with in man is indeed due essentially to a deficiency of vitamin B_1 is strikingly confirmed by clinical observations which have proved the curative action of the most highly purified preparations of vitamin B_1. .

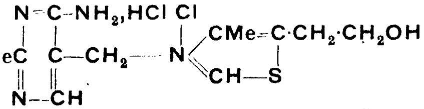
In practice beri-beri can be prevented by the substitution of unpolished for polished rice, or by the addition to the dietary of such sources of vitamin B_1 as, for example, rice polishings, wheat germ (or whole-meal wheat flour), and (in more general terms) by the use of a better quality mixed diet.

In certain parts of the world beri-beri has been astonishingly prevalent, *e.g.* in 1872 40% of the force of the Japanese navy suffered from it ; in 1898 over 4,000 cases were recorded in prisons in Java ; in 1914 900 cases per annum in infants (95% mortality) in Manila. British troops developed it at the siege of Kut in 1916. It appears to be now declining in most regions, but is still prevalent, for example, in parts of India and Japan.

In experimental animals, beri-beri, or " polyneuritis," has been studied principally in rats, pigeons, and fowls. It has been described also in monkeys, cats, dogs, and mice and other species. The characteristic abnormalities, apart from the loss in weight and wasting due to the lowered food intake, are a peripheral nerve atrophy (the so-called " polyneuritis "), and, in the final stages of the disease, paralysis and convulsions or, in the case of pigeons or hens, opisthotonus (head retraction). Atony of the gastro-intestinal tract is also a fairly constant feature. Certain typical beri-beri symptoms appear to be associated with a long-continued partial deficiency (hypovitaminosis) rather than a complete deprivation of the vitamin (avitaminosis).

Continual but slow progress was made over a period of years by a large number of workers in the very difficult and laborious task of concentrating the anti-beri-beri vitamin. Rice polishings or yeast have been the usual raw material. The principal means employed in the attempted isolation included: precipitation successively by such reagents as phosphotungstic acid, silver salts, picric acid ; adsorption on acid clay, charcoal, silica gel and the like ; solution in moist or acid alcohol. The following list gives the names of a number of investigators, each of whom succeeded in obtaining a somewhat more active material than his predecessors (the " pigeon dose " of Suzuki's concentrate was 5 mg., and of Jansen and Donath's about 0·005 mg.): Suzuki, 1912; Funk, 1913; Seidell, 1924; Kinnersley and Peters, 1925; Jansen and Donath, 1926. Jansen and Donath (1926 and later) isolated the vitamin as the crystalline hydrochloride. This was at first given the formula $C_6H_{10}ON_2$, but later work by Windaus and collaborators (1932) showed it to be a sulphur-containing substance. The formula now given to the vitamin is $C_{12}H_{16}N_4OS$. The conclusion that Jansen and Donath's preparation was the pure vitamin was strengthened by the fact that all later attempts at isolation, whether by Windaus, by Peters, by Odake or others, and using either yeast or rice polishings as alternative raw materials, have always led to a material virtually identical with that previously obtained by Jansen and Donath.

A tentative formula was put forward by R. R. Williams (1935–1936), according to which the molecule of the vitamin is built up by the combination of an amino-pyrimidine with a thioazole ring system, the former being responsible for the more weakly ionising basic group, and the latter for the stronger as well as for the " pseudo acid " behaviour (features indicated by the titration curve: Birch and Harris, 1935; Ogston and Peters, 1936; R. R. Williams and Ruehle, 1935).



Vitamin B_1 Dihydrochloride (Williams's Formula, 1936).

Previously to the actual isolation of the vitamin many facts had been elucidated about its physical and chemical properties. It was known to be readily dialysable, and of relatively low molecular weight; to be soluble in water, moist or acid (HCl) alcohol, but not in absolute alcohol, and insoluble in fat solvents ; and to be adsorbed on fuller's earth, charcoal and certain other substances—to a varying degree depending on a variety of circumstances. It is rapidly destroyed at temperatures above 100°, particularly in alkaline reactions ; but presumably is relatively little affected by ordinary commercial canning operations. It is stable to many oxidising and reducing agents (Peters, 1928).

To assay materials for vitamin B_1, graded amounts are administered to pigeons or rats suffering from the avitaminosis, and the amount is determined which is needed to effect a cure of the symptoms for a given length of time, or to bring about a given growth response ; or a preventive method may be used. The effect is compared with that given by a standard material (League of Nations International Standard, 1931) and the result expressed in international units.

Vitamin B_1 is widely distributed, but in moderate amounts only, in most natural foods. The richest sources include yeast, the germ of cereals, eggs. White bread contains inappreciable amounts, but it is present in wholemeal bread, or in bread enriched with the germ. Certain micro-organisms can synthesise the vitamin, *e.g.* in the rumen of cows, or during the process of " refection " in rats. (Refection is the spontaneous cure of vitamin-B deficiency in rats fed on a vitamin-B-free diet, as a result of the action of bacteria on crude undigested starch in the intestines ; Fridericia, 1925.) In contrast with vitamins A and E, vitamin B is not stored to any considerable extent in the body.

Until recently little was known about the mode of action of vitamin B_1 ; but it is now believed to be concerned in carbohydrate metabolism (as first suggested by Funk), probably in disposing of the lactic acid produced by bodily activities. This accumulation of lactic acid in the avitaminosis is probably the cause of the bradycardia seen in vitamin-deficient rats—a phenomenon now made the basis of a convenient method of assay—(Drury, Harris, and Maudsley, 1930 ; Birch and Harris, 1934 ; Baker and Wright, 1935) and of the head retraction in pigeons (*see* Kinnersley and Peters, 1930). As Peters and his collaborators have proved (1933), the chemical action of vitamin B$_1$ on carbohydrate metabolism may be studied *in vitro*. Attention has recently been drawn to abnormalities in the oxidation not only of lactic but also of pyruvic acid in vitamin-B$_1$ deficiency. L. J. H.

B VITAMINS. B$_1$ vitamin (*v. supra*); vitamin B$_2$-complex ; vitamins B$_3$, B$_4$, B$_5$, B$_6$, *v.* VITAMINS.

BABBITT METAL. A bearing or anti-friction metal, containing in its original composition 88·9% tin, 7·4% antimony, and 3·7% copper. The usual proportions of the constituent metals now vary between 80 and 90% tin, 5 and 15% antimony, and 3 and 10% copper.

BABLAH or NEB-NEB. Commercial names for fruits of several species of acacia; used in the East in combination with alumina and iron mordants to produce various shades of drab and fawn colour in calico-printing. East Indian bablah is largely obtained from *Acacia arabica* (Willd.) (*A. indica* (Benth.)) ; Senegal and Egyptian bablah largely from *Acacia arabica* (*A. nilotica* (Delil)). The aqueous extracts contain a red colouring matter together with considerable quantities of gallic and tannic acids. (*v.* ACACIA.)

BABUL GUM. An inferior kind of gum arabic from *Acacia arabica* (Willd.). Known also as "Bengal gum" or "Gond babul."

BACO *v.* BASSIA FATS (ABAKU NUTS).

BACTERIA, CHEMICAL ACTION OF *v.* FERMENTATION.

BADDELEYITE. Native zirconium oxide, ZrO_2, crystallising in the monoclinic system. A few isolated crystals have been found in the gem-gravels of Ceylon, and a more abundant supply of small crystals was met with at about the same time in the iron mine of Jacupiranga, in São Paulo, Brazil. The latter, at first described under the name brazilite, occur as an accessory constituent of a magnetite-pyroxene rock called jacupirangite, which is associated with the deposits of magnetite. The crystals from Ceylon are black and opaque, with sub-metallic lustre, but small splinters are transparent and yellowish in colour ; sp.gr. 5·72–6·025 ; ZrO_2 98·9%. The smaller crystals from Brazil range from colourless to brown ; sp.gr. 5·5 ; they contain ZrO_2 96·52%, with small amounts of silica, alumina, ferric oxide, lime, etc. The mineral has also been identified in a rock resembling jacupirangite in the iron mines of the island of Alnö, Sweden. More recently, minute crystals have been detected in a sanidine bomb rich in zircon from Monte Somma, Vesuvius, in a corundum-syenite from Bozeman, Montana, and in the concentrates of gold-washings at Kilo, Belgian Congo.

A massive form of zirconia occurs much more abundantly in the Serra de Caldas region of Minas Geraes, Brazil, a region characterised by the occurrence of nepheline-syenite rocks. Pebbles of compact material are here found in the diamond washings, and are known to the diamond miners as "favas" (meaning "bean" ; other "favas" consist of titanium dioxide). These are pale-brown, slate-grey or blackish in colour, fine-grained and hard. Sp.gr. 4·6–5·4 ; they contain ZrO_2 73–93%, the principal impurity being silica, with some iron, alumina and titanium. In the same region there has also been found, as a crust on weathered augite-syenite, mamillated or reniform masses with a radially-fibrous structure and concentric banding, it contains ZrO_2 97%, and has sp.gr. 5·538. This variety appears to occur in considerable quantity, and in lumps weighing several kilograms. E. Hussak, in 1899, referred the massive form occurring as "favas" to baddeleyite, but he was inclined in 1903 to regard the fibrous variety as a distinct modification of zirconia. The latter has recently been sold in America under the trade name *zirkite*, and it is stated to consist of a mechanical mixture of baddeleyite, zircon and a new zirconium silicate. The mineral possesses a high degree of infusibility, high resistance to basic and acid slags, low thermal conductivity and a very low coefficient of expansion. It is thus eminently suitable as a refractory material for the construction of crucibles, muffles, fire-bricks and furnace linings. It is also employed as an opacifier and as an abrasive. (W. T. Schaller, "Mineral Resources," U.S. Geol. Survey for 1916, 1917, ii, 377 ; A. Granger, Chem. News, 1919, **118**, 115 ; B. von Freyberg, "Die Bodenschätze des Staates Minas Geraes," Stuttgart, 1934). L. J. S.

BADISCHE ACID. [α-]*Acid.* β-Naphthylamine-8-sulphonic acid,

$$C_{10}H_6(NH_2)SO_3H$$

BAEL FRUIT. The dried half-ripe fruit of *Ægle marmelos*, from Malabar and Coromandel ; it is rich in tannins and used in diarrhœa and dysentery, the fresh pulp sometimes being employed as a laxative.

BAEUMLERITE. A potash-salt mineral found as thin bands in the rock-salt of the Desdemona salt mine in the Leine Valley, Prussia (O. Renner, 1912). It is colourless, transparent and extremely deliquescent, and has the composition $KCl{\cdot}CaCl_2$. F. Zambonini (1912) has suggested that this is identical with the Vesuvian mineral "chlorocalcite," first described by A. Scacchi in 1872 and later proved to be cubic and with the composition $KCl{\cdot}CaCl_2$. L. J. S.

BAGASSE, BEGASS, or MEGASS. Damp sugar-cane fibre disintegrated by passage through crushing and squeezing rollers in order to extract the sugar juice.

BAICALIN, $C_{21}H_{18}O_{11}$, m.p. 223°, $[\alpha]_D^{18}$ $-144{\cdot}9°$, is one of two known glycosides which yield on hydrolysis glucuronic acid, the aglucone in this case being 5 : 6 : 7-trihydroxyflavone (Shibita, Iwata and Nakamura, Acta Phytochim. 1928, i, 105). It is obtained from the roots of *Scutellaria baicalensis* and is not hydrolysed by emulsin or the known β-glucosidases. It is, however, attacked by an enzyme which can be extracted from the roots with 70% glycerol and which does not act on other β-glycosides. It does, however, hydrolyse scutellarin, which is 4′-hydroxy baicalin (Miwa, Acta Phytochim. 1932, **6**, 155), and is present in the leaves of the same plant. This occurrence of one compound in the roots and another, with an additional hydroxyl, in the leaves of the same plant is remarkable. E. F. A.

BAKANKOSINE *v.* STRYCHNOS ALKALOIDS.

BAKELITE (trade name). This name is applied to a large number of products consisting wholly or in part of phenol-formaldehyde condensation products which are manufactured by Messrs. Bakelite Limited (Great Britain) and the Bakelite Corporation (U.S.A.). These products include phenol-formaldehyde moulding powders, phenol-formaldehyde bonded sheets, rods and tubes, insulating and protective lacquers, cements and oil-soluble resins (for varnish manufacture). *See* PHENOLIC PLASTICS.
E. E. W.

BAKERITE. A hydrated borosilicate of calcium, $8CaO\cdot5B_2O_3\cdot6SiO_2\cdot6H_2O$, containing B_2O_3 27·7%. It is massive and snow-white, sometimes with a greenish tinge, and resembles unglazed porcelain or fine-grained marble in appearance. D 2·73–2·93, H 4½. It occurs with howlite as veins and nodules of considerable size in the borate mines in the Mohave Desert, sixteen miles north-east of Daggett, in San Bernardino Co., California (W. B. Giles, Min. Mag. 1903, **13**, 353). L. J. S.

BAKHAR. An artificial ferment prepared from rice, powdered roots, and other parts of certain plants by Indian natives and used in the production of Hindu rice beer (pachwai) and of the spirit distilled from it. It contains many varieties of *Mucor* capable of saccharifying starch, the most active being *Aspergillus Oryzæ*. It also contains several alcohol-producing yeasts. Hutchinson and Ram Ayyar (J.S.C.I. 1916, **35**, 751) determined the fermentation power of bákhar from different parts of India by finding the volume of alcohol produced from 100 g. of steamed rice and 1·5 g. of the ferment. They state that this varied from 46·3 ml. to 61·6 ml. The strength of the alcohol is not given, but was probably expressed in terms of absolute alcohol. This yield is much lower than that obtained under similar conditions with the "kòji" ferment from Japanese rice beer, which is practically a pure culture of *Aspergillus Oryzæ*. F. G. H. T.

BAKING POWDERS. Baked goods can be aerated not only by yeast but also by the use of certain chemical ingredients which are known as baking powders ; in this case the carbon dioxide is generated by chemical action. The alkaline ingredient is almost invariably sodium bicarbonate, which, incidentally, is readily obtained in a high degree of purity. This is acted upon by an acid in order to generate the carbon dioxide, and there is a considerable choice with respect to the acid ingredient. At one time tartaric acid was popular and then later cream of tartar (potassium hydrogen tartrate) was used and is still in use. Cream of tartar has the advantage over tartaric acid of not acting to any great extent on the bicarbonate until it receives the heat of the oven. This enables a dough containing it to be kept some time before baking, which is often a matter of great convenience. For ordinary baking powder two parts of cream of tartar to one part of sodium bicarbonate is usually advocated, the whole, of course, being diluted down with starch or flour.

Another acid ingredient which is increasing in popularity is acid calcium phosphate, and this, like cream of tartar, has only a slight action on the bicarbonate present previous to setting in the oven. In recent years sodium pyrophosphate is also being employed. In America sodium aluminium sulphate has been used in certain baking powders despite the criticism raised in some quarters as to the desirability of this use of an aluminium compound. In making baking powders the acid ingredient and the sodium bicarbonate are usually diluted down with maize starch. For cake making, etc., the housewife takes, for example, one to two teaspoonfuls of baking powder per pound of flour.

This matter has been followed to its logical conclusion by supplying the housewife with what is known as self-raising flour, that is to say, flour which contains the self-raising ingredients in the correct proportion so that it may be used directly. Such self-raising flours are commonly made by millers and in this case the acid ingredient generally employed is acid calcium phosphate, although cream of tartar and sodium pyrophosphate are not unknown. A popular formula for the making of self-raising flour is the admixture to one sack (280 lb.) of a fairly soft flour of not too high moisture content, of 4½ lb. of high-acidity acid calcium phosphate and 3 lb. of sodium bicarbonate. When using acid calcium phosphate for the making of self-raising flour it is important to remember that, in commercial practice, two grades of acid calcium phosphate are made, one having an effective acidity of 50 to 60 units and the other having an effective acidity of 80 units. The higher strength acid phosphate is the one normally employed. The neutralising power (effective acidity) of an acid phosphate is usually reported in terms of sodium bicarbonate, that is, is returned as the number of parts of sodium bicarbonate neutralised by 100 parts of the acid phosphate.

For certain goods in bakeries ammonium carbonate, known as "vol," is employed. This gives off ammonia and carbon dioxide in the oven and thus causes aeration. It is rarely, however, that more than a pinch of "vol" is advocated, as excess is likely to give rise to unpleasant tastes and smells.

Another method is used for producing the "soda bread" which is popularly made in Ireland. Probably over 60% of the bread consumed in Ireland is of the non-yeast type and is made by adding to the flour sodium bicarbonate and sour buttermilk. The dough is made in a slack condition and placed in a warm iron pot and baked immediately. As the buttermilk varies so much in acidity it is the usual practice for millers to add to such flour some acid calcium phosphate to ensure that there is excess of acidity to liberate all the carbon dioxide from the bicarbonate. On no account must excess bicarbonate be left in the loaf, as this causes darkening of the crumb and an unpleasant smell and flavour. Irish soda bread is distinctly "heavier" than yeast-fermented bread.

Much work has been done on the neutralising value of acid calcium phosphate, and attention is drawn to the following references: Bailey (J. Assoc. Off. Agr. Chem. 1925, **8**, 444, 490; 1926, **9**, 253); Wadman (Ind. Eng. Chem. 1921, **13**, 1146); and Herd (Cereal Chem. 1927, **4**, 349). The evaluation of baking powder has also been investigated by Chittick (J. Assoc. Off. Agr. Chem. 1927, **10**, 36; and Official and Tentative Methods of Analysis of the Assoc. Off. Agr. Chem. 1925, 301). D. W. K.-J.

BALAM FAT *v.* BORNEO TALLOW.

BALANCE.[1] A generic term, designating a variety of machines for ascertaining the weight of a body in terms of the weight, at the time and place, of a standard *mass* (gram, ounce, pound, etc.). By means of a balance and a set of "weights," we ascertain that a body has P times the weight of the unit piece of the set, and conclude that its mass is P times the mass of this piece likewise, whatever the chemical nature of the body may be. In justification of this inference we might refer to Newton's pendulum experiments, or to the often proved chemical axiom that the weight of any body or set of bodies is independent of the state of combination of its elements. But from the standpoint of the chemist it is sufficient to know that, supposing even each element had its own factor for converting "weight" into mass, it would for all practicable purposes still follow that the weight of a body, however complex, is equal to the sum of the weights of what in any sense we may call its "components," and that the ratio of the weight W_1 of a body of fixed elementary composition to the weight W_2 of another body of even a different fixed composition is as constant, although perhaps not equal to the ratio of the masses $M_1 : M_2$. Of all balances the equal-armed lever balance, often called "*the* balance" *par excellence*, is by far the most important.

The balance exists in a variety of forms, all of which seek to realise the same ideal machine. An absolutely rigid beam, so suspended that whilst it can rotate freely about a certain axis (which goes across it somewhere above its centre of gravity, and of which every point holds a fixed position in reference to the stand) it is not capable of any other motion. From two points, A and B, which lie in the same plane as the axis of rotation—one near the left, the other near the right end of the beam—the pans are suspended by means of absolutely flexible linear strings. A and B are equidistant from the axis of rotation. So far all balances are alike. In now passing to the actual instrument, we shall confine ourselves in the main to the class of balances known as precision balances.

Most balance makers prefer the form of a largely-perforated rhombus or isosceles triangle, cut out of a plate of metal, and thus attain all that is needful without offending the eye by unduly stretching the middle section, and without using anything more intrinsically rigid than hammered brass or some kind of bronze. In reference to ordinary chemical balances (for charges up to, say, 100 g.), it would be no great exaggeration to say that any reasonably made beam is sufficiently rigid; only in the case of balances intended for very high charges, such as 5–10 kg., is it at all worth while to employ refinedly designed beam-forms, or to look out for a material of exceptionally high rigidity. For these particular balances hard steel would be the best material; but, unfortunately, steel beams are apt to become magnetic. With small assay-balances intended for charges up to, say, 5 g., on the other hand, the question of rigidity is practically out of court, and the use of an exceptionally light material—such as aluminium, or, better, that alloy of 95 parts of aluminium and 5 of silver which Sartorius of Göttingen uses for small balances generally—is indicated. In all balances the axis of rotation is realised in a straight knife-edge ground to a prism of hard material, which is firmly fixed to the beam, traversing it crosswise and resting on a hard bearing. In ordinary balances the middle knife is simply driven through the beam, and only its two ends are supported in cylindrical, or, what is better, roof-shaped bearings, which form secures to the edge a sufficient fixity of position, forward and back sliding being prevented by cutting off the ends of the knife obliquely, so that the edge terminates in two points, and closing the bearing at each end by a steel plate, so that the knife has just room between without jamming. In suspended balances the central bearing is fixed at the lower end of a light framework, terminating above in a hinged-on ring for suspending the instrument from a fixed hook or the thumb of the operator.

In all precision balances the central bearing is attached to a fixed pillar, and is plane; in the best balances the bearing is made of one piece, and the central knife-edge rests upon it in its entire length. A plane bearing necessarily involves an arrestment so constructed that, besides doing its primary duty, it assigns to each point of the central knife-edge a fixed position on its bearing. In former times hard steel was used exclusively for both knives and bearings; subsequently agate bearings came to be combined with steel knives. Robinson of London was the first to make both knives and bearings of agate. The agate knife adds nothing to the precision of a newly-made balance, but it always remains clean, while a steel knife, in a chemical laboratory more especially, is apt to rust. Steel knife-edges are generally ground to an angle of 60° (or 90° for very heavy charges). In agate knives, as made by Oertling, only the body of the agate prism is ground to 60°, while the edge is formed by two narrow facets, inclined to each other at a far more obtuse angle. Such an obtuse edge stands many years' constant use without wearing out.

---

[1] The first section of the article **BALANCE** was written by Professor W. Dittmar, LL.D., F.R.S., Professor in Anderson's College, Glasgow, for the first edition of the Dictionary, which appeared in 1890. It is such an admirable historical account of the subject that we have thought fit to include it in the present position in an amended form. In the later part of the article the structure of the balance and matters connected therewith have, at our request, been described very fully by Dr. Manley. It was thought that if circumstances should require the erection of a balance from material to hand in a moderately equipped laboratory in a remote district, full details might be found of use.
Editors.

For the realisation of the two point-pivots A and B, a great many combinations have been invented. In ordinary balances, as a rule, a vertical slit is cut into each end of the beam, and this is traversed by a short prismatic knife, the edge of which is a circular arc of small radius which stands perpendicular to the line AB. From each such knife the pan is suspended by means of either an 8- or a 2-shaped steel hook. This construction, if well executed, may afford high precision, but the suspender-hook is apt to rub against the sides of the slit in the beam and in modern balances it is rarely seen; in these, as a rule, the pans are suspended from long straight knife-edges, similar to the central one, by means of broad bearings which, of course, must be arranged so that they neither turn nor slide. A very efficient and easily made arrangement is to give the bearing the form of a roof cut out of one side of a prismatic block of steel or agate, and to fix it to the upper end of a stirrup-shaped or 7-shaped holder which terminates below in an eye, from which the pan is suspended by a suitable hook. The eye stands at right angles to the knife-edge ; its working point, when the instrument is in use, lies vertically below the centre of the respective end-edge, and the effect is the same as if the whole of the load were concentrated in that one centre-point, although the pressure of the bearing on the knife is equally distributed over the whole of its working length. This hook-and-eye arrangement is absolutely indispensable if the pans are suspended by stiff stirrups, because, if these were rigidly connected with their bearings, the virtual point of application of the load would shift forwards and backwards on the edge, and the least want of parallelism between it and the axis of rotation would cause the balance to give inconstant readings.

These roof-shaped bearings were formerly used almost exclusively by German makers, although an undoubtedly superior system had been introduced successfully by Robinson of London many years ago. In it the pans are suspended by *plane* bearings which a suitable extension of the arrestment keeps in their right positions. Robinson's balances were justly famous in Great Britain—a few of them are still working to this day—yet, after Robinson's death, Oertling was almost the only balance maker who followed him in this respect. The general plea against the system was that flat end-bearings were subject to rotational movements; and some, after having adopted Robinson's plan, "improved" upon it by cutting out a central portion of each end-knife, so that it worked only with its two ends ; proving thereby that they did not understand their business, because a *really plane* bearing, as a matter of fact, does *not* rotate on a *really straight* knife-edge, even if the pan oscillates strongly. The principal advantage of the Robinson system is that it enables one to do what the roof-shaped bearing prohibits, namely, to satisfy oneself that the knives and bearings are geometrically perfect. But here, as in all analogous cases, we must not forget that the excellence of an instrument—supposing it to be based on a reasonable system—depends far more on the skill of the maker than on the theoretical perfection of the design.

From the bare realisation of the ideal machine, we now pass to the accessories which a balance needs in order to become a convenient instrument, and we will consider these in the order of their importance.

The arrestment is a mechanical contrivance to enable the beam to be arrested at any point of its angular motion, and to bring it to permanent rest in its "*normal*" position, in which the plane of three axes is horizontal. If the three pivots are self-adjusting, there is, strictly speaking, no need of an arrestment ; still, for the rapid execution of precise weighings it is wholly indispensable.

If the central bearing forms part of a suspended frame, an arrestment is easily devised in the way illustrated by Fig. 1. Here it will be seen that the balance is hinged to the bent-down end of a flat bar which slides up and down in guides fixed to the pillar between two sets of rollers and a spring. At its lower end the bar has a small wheel which rests on the shorter end of the hinged lever by means of which the balance is raised or lowered. A small vertical adjusting screw below the shorter end of the lever defines the lowest position of the bar at which the pans just touch the table without slackening the chains. It is an improvement to suspend a heavy block of metal at the lower end of the frame, to compel it to hang plumb, and to hinder it from oscillating. The specific advantage of *suspended* balances is that they need no horizontal table or levelling screws at the board on which they may be erected. But pillar-balances are on the whole more convenient. In the case of these (supposing plane bearings to be absent) a good system is to fix the central bearing to the top of a rod which slides up and down within the pillar—properly guided to prevent shaking and

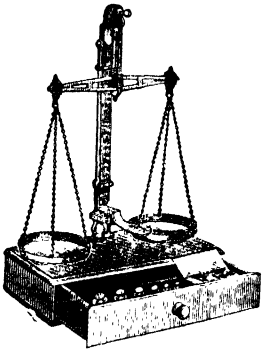


Fig. 1.

rotatory motion—with its lower end resting on an eccentric concealed in the sole and governed by a lever- or disc-shaped handle. The eccentric must be so adjusted that when it is at one of its extreme positions, the pans just touch the board and no more, while, when it is in its other extreme position, the beam is at its maximum angle of free play. In the excellent *Tarierwaagen* of Messrs. Becker's Sons, Rotterdam, this system of arrestment is realised to perfection and needs only to be slightly modified to adapt itself to the case of a plane central bearing. An Oertling balance having *three* plane bearings and for charges up to 5 kg. is depicted in Fig. 2.

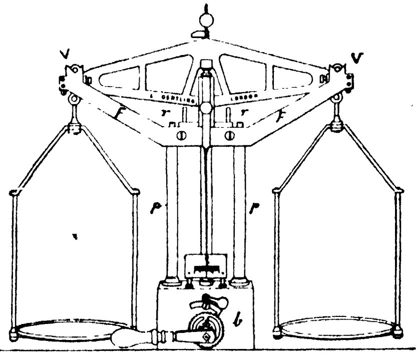


FIG. 2.

The instrument rests on three pillars standing on a hollow square block of iron which conceals the eccentric. Firmly fixed to the top ends of the pillars is a substantial brass frame which terminates at its two ends in V-shaped supports for the end-bearings. These latter are agate plates cemented each to the horizontal bar of a kind of stirrup, the bar terminating on each side in a cylindrical steel pin which, when the balance is at rest, lies in the corresponding V of the frame. The central pillar conceals a movable steel rod, provided at its lower end with a wheel which rests on the eccentric. Its upper end carries a substantial brass block which divides into two short piers above, whilst it expands below into a horizontal plate, pierced by a circular perforation near each end. These perforations exactly fit two cylindrical steel pins, *r*, *r*, fixed to the top plate of the pillars, so that the rod, when moving up or down, cannot turn or shake in the slightest degree. The space between the two piers is bridged over by the central bearing, a plane agate plate fixed to a prismatic piece of brass, which is dovetailed into the tops of the piers, so that, while perfectly steady when in its place, it can without much effort be slid out or in (Fig. 3). It is inserted while the beam is being held in its intended position and passes through a large perforation in the beam into which the middle knife projects. The beam terminates at its left end in one, at its right end in two, horizontal steel pins whose shoulders are continuous but rapidly expanding surfaces of rotation, and these pins fit, the single one into a notch, the couple into a fork, forming part of the fixed arrestment frame. In the arrested balance each bearing is almost in contact with its knife; if the eccentric be now turned, the central bearing rises and lifts the whole, beams and end-bearings, to a greater or less height, and ultimately into that maximum height at which the eccentric stands still without being *held* in its position. If the eccentric be now turned the other way, both the beam and the end-bearings fall back, ultimately, into their prescribed positions of rest, even if they should have twisted, which however, they never do in the instrument under description. For a balance intended for quick work, and more especially for one used occasionally for the weighing out of predetermined quantities of solids or liquids, this system of arrestment is the best that we know of, because it enables the instrument to be handled pretty much like an ordinary pair of scales; only, to be able to do so to the best advantage, and without spoiling the terminal pivots, the pans must be suspended by flexible short-linked chains whose length is so adjusted that the pans just touch the table when the balance is fully arrested. Stirrup-shaped pan-suspenders (as represented in the figure) are more convenient than chains in many respects, but, for the purpose under consideration, they do not work with plane end-bearings. The ratchet-wheel

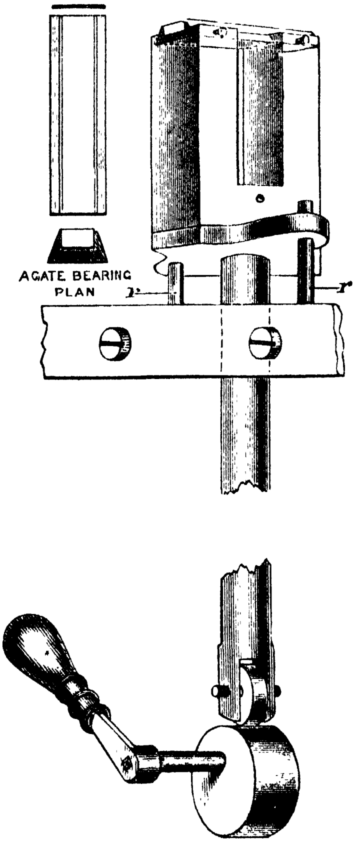


FIG. 3.

visible in the figure was intended to enable the eccentric to be arrested at intermediate positions (in taring with garnets and similar operations) but was found not to work satisfactorily ; it is simpler and better to have a block of wood so adjusted that when put under the handle it just raises the beam sufficiently to enable one to see which side goes down.

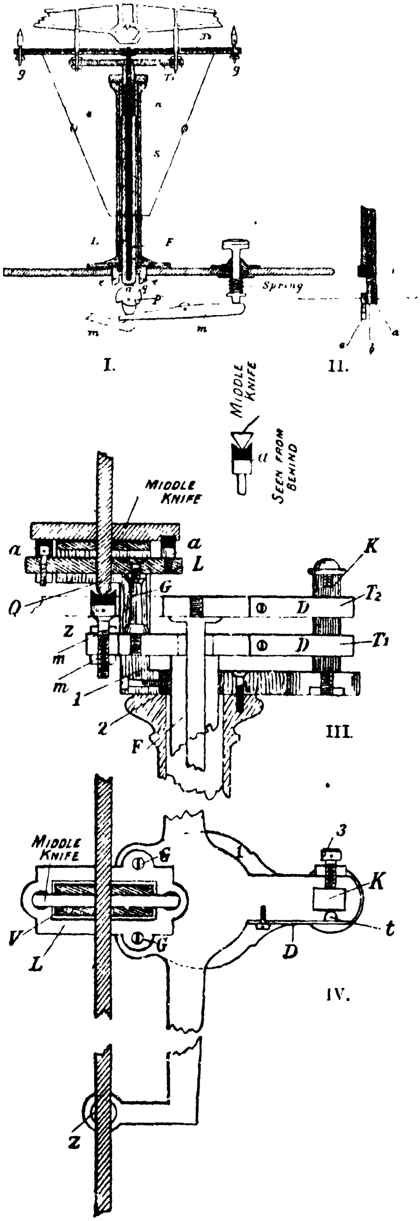


Fig. 4.

III. Section through pillar and middle knife ; IV. Horizontal projection.

Instead of fixing the arrestment frame to the pillar and making the central bearing movable, we may, of course, do the reverse, and this latter system, indeed, is generally preferred for precision balances of a higher order of accuracy, and is illustrated in the Staudinger Nachfolger balance in Fig. 4 (I to IV). The pillar is hollow and accommodates a round bronze rod F. This rod itself, however, conceals a co-axial round rod L of nickelled steel. The bronze rod F, at its lower end, is guided by perforated blocks, *e*, *e*, Fig. 4. I, while at its upper end it terminates in a thinner cylinder surrounded by a gently acting spiral spring *n*. The head of the pillar is perforated and guides the attenuated end of F in its up-and-down motion. The inner (steel) rod L is guided similarly within the bronze rod F and has a spring *i*, Fig. 4. II, about its lower end to assist its natural tendency to sink. The two rods F and L carry two independent arrestment-bars ; L the bar T_2 for the end-bearings, F the bar T_1 for the beam.

A square pillar K (Fig. 4. III and IV), which rises from a prolongation of the head of the stand pillar S, by passing through perforations in the two bars T_1 and T_2, prevents any motion of these about the axis of their rods. As shown by Fig. IV, an adjusting screw, passing through the bar, and a flat spring *t* on one side of the square perforation of the bar (T_1 or T_2) enforce steadiness of motion.

The upright pins *g*, *g* (I), which are tipped with sharp agate cones, arrest the end-bearings by rising into corresponding conical hollows in the latter. (Fig. 5, though taken from an Oertling balance, will give an idea of the way in which these pins work.) The two slanting lines O, O (Fig. 4. I) are meant to indicate two supports, which pass through slots in the pillar S and the bronze rod F, and are fixed to the inner rod L, to lend additional rigidity and steadiness of motion to the end-bearings arrestment.

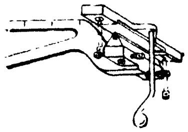


Fig. 5.

The arrestment of the beam is effected by two adjustable piers Z rising from the bar T_1 of the bronze rod. The tops of these piers carry trough-shaped agate bearings, in which the lower (bevelled) edge of the arrested beam lies. This would be sufficient to keep the beam from turning. To hinder it from moving progressively, there is a horizontal frame L (Fig. 4. III and IV) united with bar T_1 by two little pillars G, G, and carrying two agate bearings, a trough-shaped one at the hinder end and a plane one at the front end of the middle (agate) knife. The trough-shaped bearing receives that end of the middle knife as the trough-shaped bearing of an ordinary balance would (so that by it, and the two beam-supports, three points of the arrested beam are fixed in prescribed positions) ; the plane bearing in front only supports the knife as it rises up to it on arresting. This plane bearing is adjustable by means of a screw, so that the arrested central knife-edge can be made rigorously parallel to the fixed central bearing of the working instrument.

There are three eccentrics, all attached to the same axis and governed by the same handle (Fig. 4. II), one, A, for the bronze rod F, a second, B, for the inner steel rod L, and a third, C, for a pan-arrestment; their action is readily understood by an inspection of Fig. 4. I. When the handle stands so that line *p* (Fig. 4. I) is vertical the beam is arrested ; after this point has been passed, the beam-supports remain at the same altitude, but, on turning the handle further, bar T_2 is raised to lift the terminal bearings as soon as line *q* stands vertical. The last third of the motion of the handle arrests the pans.

The principal feature of the Staudinger Nachfolger arrestment obviously is the relative independence of the beam-arrestment and of the end-bearings arrestment. In most other movable frame systems there is only one frame for both, and things are arranged so that the middle edge is held fast after the end-bearings have been lifted by a hair's breadth, and that the upward motion comes to an end as soon as the middle knife is just visible above its bearing. A refinement upon this construction is merely to effect the three contacts, and then, by means of a special eccentric, to let the middle bearing drop through a distance of 0·1 or 0·2 mm.

Whilst all the several points of a rigid though movable arrestment-bar move up and down in vertical straight lines, the end-edges of the vibrating beam describe circular arcs. Hence whenever the bar is raised against the *slanting* beam, the end-bearings *tend* to slide over their knives and to spoil them. To preclude the possibility of this, Becker & Sons, in their finest balances, make the bar for the end-bearings arrestment of two halves which are hinged on to the pillar in or very near the axis of rotation. Sartorius adopted this system and brought it into a slightly different form, regarding which we refer to Bibl. 4, where it is illustrated by a drawing.

In a balance which has only plane bearings, no kind of arrestment, of course, will give satisfaction, unless its several parts, and also the pillar and the sole, are sufficiently substantial to ensure absolute constancy of configuration and absolute steadiness of motion even after long-continued use. The old masters used to pay great attention to this important point, but it is sadly neglected by the majority of their present successors.

In a balance of which the end-pivots are self-adjusting, the movable arrestment frame assumes a very simple form. All that is needed is a small frame bearing V-shaped notches for arresting the middle knife in a prescribed position, and fixed to a horizontal bar with two projecting pins, in order, at the same time, to support the beam in a horizontal position. As these pins have no other function, the bar may be very light, and the whole system need not have that absolute steadiness of motion which is indispensable in the case of plane end-bearings.

The needle and scale serve to define the angular position of the beam. In all modern precision balances the needle points downwards, and is meant to embody a straight line passing through the axis of rotation and standing perpendicular on the line connecting the two point-pivots A and B. The scale is attached to the pillar ; its zero, if the stand is properly levelled, lies vertically below the axis of rotation. To enable the stand to be levelled, there must be either a plumb line or two spirit levels *fixed to the pillar*, and so adjusted that when they point to their zeros, the line connecting the zero of the scale with its projection on the middle edge is vertical. The scale should be so graduated that the needle-line, if produced, would cut, not the circle described by the needle's reference point, but the horizontal tangent to this circle, into pieces of equal length (*v. infra*). In most practical cases, however, this comes to the same as saying " into pieces of equal angular value." In balances provided with a fixed arrestment frame the scale should be made to move up and down with the beam, so that its position in reference to the needle remains constant. In most balances the end-point of the needle is just clear of the upper circular edge of the scale, but it is better to make its lowest portion almost linear, and let this project over the scale and almost touch it.

The rider.—Small weights are difficult to handle and easily lost. To avoid this inconvenience, Berzelius conceived the happy idea of dividing the right side of the beam, or rather the horizontal lever arm corresponding to it, into ten equal parts, and substituting one rider weighing ten centigrams for all the centigram and milligram pieces of the set of weights. Obviously the rider, when suspended at the first, second, etc., mark from the centre, acts like 1, 2, etc., centigrams placed in the pan, and it is equally obvious that every tenth of a division on the beam corresponds to one milligram of additional weight. This system was universally adopted and is still in use, only with this qualification, that we now apply it to the counting of the milligrams by means of a rider weighing ten milligrams. The reason for the change is obvious. In most balances the points 0 and 10 of the rider-scale are inaccessible. Becker & Sons avoid this inconvenience by dividing the arm into twelve parts, and supplying a rider weighing twelve milligrams. Other makers, for instance, Messrs. Verbeek & Peckholdt, of Dresden, make the top bar of their beams exactly horizontal, and, besides keeping it clear of impediments, make it project beyond the terminal edges. One of the advantages of this system is that, in the case of a short beam, it enables us to double the degrees of the rider scale, by dividing each arm into only five (integer) parts, numbering these from the left knife onwards and usnig a rider weighing five milligrams. Only, if we do so, the rider suspended at the zero must be considered as part of the instrument. Bunge provides a special rider-bar so contrived that the path of the rider lies in the plane of the three axes. This, *theoretically*, is the most perfect arrangement.

A rider arrangement, to be complete, must be supplemented by a mechanical contrivance enabling one to shift the rider while the balance case is closed, and to do so with greater rapidity, ease, and certainty than would be afforded by the use of forceps, supposing the case to be open.

The gravity bob—a small button or disc of metal so attached to a wire standing vertically on the top of the beam exactly above the axis of rotation that it can be screwed up and down along the whole range of the wire. It enables one to raise or lower the centre of gravity of the beam, and thus to establish any desirable degree of sensitivity.

A bob thus constructed meets all the requirements of the balance maker, but for the chemist who uses the balance it is desirable to have an arrangement which enables him at a moment's notice to establish any predetermined degree of sensitivity. Such an arrangement was invented by the writer some years ago (Bibl. 8 and 5). It consists of a small bob fixed by mere friction to the upper end of the needle, which at that part has the form of a triangular prism, and is provided with a graduation. The mode of standardising the scale is explained below.

Some arrangement for establishing perfect equilibrium in the unloaded instrument is required. A small bob screwing along a horizontal wire fixed to some convenient part of the beam answers best. Less convenient is a "vane," meaning a little movable horizontal lever attached to the lowest point of the wire; which carries the ordinary gravity-bob, or to the upper part of the needle.

The Theory of the Balance.

For a first approximation imagine a balance which is ideally perfect, and assume it to be charged with P grams from the left and with P grams from the right point-pivot. The balance, when free to vibrate, can remain at rest only in its normal position, and if brought out of it will vibrate about it as a pendulum, because the two charges are equivalent statically to one heavy particle weighing 2P, situated in the central knife-edge. Now, put a small overweight $\triangle$ on, say, the right pan; the position of potential rest will shift, and the beam, to reach it, must turn (downwards on the right side) through a certain angle a, which depends only on $\triangle$ and on the weight W of the empty beam, which latter we may assume to be concentrated in its centre of gravity C, the force 2P being obviously out of consideration. But the two weights, $\triangle$ at b and W at C, are equivalent to a point weighing W+$\triangle$ and lying on the straight line Cb at a point C′, not far from C. The new position of rest is gained as soon as C′ lies vertically below the axis of rotation, or, to put it in other words, the right side of the beam goes down until the leverage of $\triangle$ is so far reduced and that of W has so far increased that the two *momenta statica* are equal to each other.

Imagine now the axis of rotation to be shifted vertically upwards through a small height h, and parallel to itself. The imaginary point weighing 2P now, as soon as the beam turns, *has* a lever and helps the weight W; the beam will turn through a less angle a' to gain its new position of rest, and, supposing 2P to increase, a' becomes less as 2P increases.

Imagine now the axis of rotation to be shifted downwards towards the centre of gravity. The heavy point weighing 2P grams now helps $\triangle$, and the angle which separates the two positions of rest will become greater than the original angle; the greater 2P the greater will be the actual angle a''. But the two weights, W concentrated in C, and 2P concentrated in the centre of the line ab, taken jointly, are equivalent to one point C′ weighing W+2P grams, and situated on the straight line connecting the two points; and supposing 2P to increase gradually from zero onwards, C′, in the second case, will rise and rise, and at a certain value of 2P fall into the axis of rotation. The balance then has no definite position of rest; and if C′ rises still higher, the balance upsets. However small an overweight $\triangle$ may be put on either side, the beam would have to turn upside down to reach its one (theoretical) position of stable equilibrium.

The balance maker, of course, takes care so to adjust his instrument that even if the sensitivity is at the highest value which the balance is meant to afford, and the two-sided charge 2P at its maximum likewise, the centre of gravity of the whole system lies on the safe side of the axis of rotation.

Assuming this condition to be fulfilled, the balance to be exactly equal-armed and to be charged with a pan weighing p_0 grams and a load of p grams on each side, the angle a of deviation is governed by the equation:

$$tga = \frac{\triangle l}{Ws+2(p_0+p)h} \quad . \quad . \quad . \quad (1)$$

where l stands for the arm-length, s for the distance of the centre of gravity of the empty beam from the axis of rotation, and h for the distance of the axis of rotation from the plane of the two end-edges, the axis being assumed to lie *above* the plane. In the opposite case h must be assumed to be negative, or the *plus* sign before the second term in the denominator be replaced by a *minus* sign. But tga is the ratio of the absolute length of scale (measured tangentially, *v. supra*) corresponding to angle a to the distance I of the tangent-zero from the axis of rotation. Hence we have

$$n = \frac{\triangle l\mathrm{I}}{Ws+3(p_0+p)h} = \triangle\,.\text{“E”}. \quad . \quad (2)$$

where, supposing I to be measured in tangential scale degrees, n may be read as meaning the number of degrees through which the needle turns in consequence of the addition of $\triangle$. The product condensed into "E" we will call the "sensitivity."

The reciprocal of E, *i.e.* the number $\mathrm{E}^{-1} = \frac{1}{\mathrm{E}}$, is the weight-value of 1 degree of the scale—*i.e.* the particular $\triangle$ which makes $n=1$. With a precision balance the milligram is a convenient unit for $\triangle$.

For a balance provided with the writer's auxiliary bob, eq. (2) may conveniently be brought into the form

$$\frac{\triangle}{n} = \mathrm{E}^{-1} = \frac{(Ws+2Ph)+b(y_0+y)}{l\mathrm{I}} \quad . \quad (2a)$$

where b is the weight of the bob and y_0+y the distance of its centre of gravity from the axis of rotation y_0, being that distance which prevails when the bob is at its highest (zero) position.

In a well-made balance the influence of P on E is small ; we may therefore assume the P of the equation to be some average value, and, contracting constants, say, the weight-value of one degree is

$$E^{-1}=A+By \quad . \quad . \quad . \quad . \quad (3)$$

where A and B are constants ; A obviously being that value which E^{-1} assumes when $y=0$. – B is easily determined by one trial at y at its maximum, and the scale thus standardised.

The theory of the rider might be allowed to take care of itself if, in general practice, the rider's path exactly coincided with the plane of the three axes But such is not the case ; this path, as a rule, lies above the plane, and each mark at its own altitude H. Let us therefore assume that, after the balance had been charged with P on each side, a rider weighing p had been suspended at a point of the beam corresponding to the fraction kl of the arm-length (at the $(10k)$th mark counting from the centre). If the beam stand horizontal, and a weight kp be placed in the opposite pan, the beam will remain in equilibrium, because we have $l(pk)=p(kl)$ whatever H may be ; the rider where it is and the charge kp (virtually) in the left knife-edge are conjointly equivalent to a fixed point weighing $kp+p$, and situated on the straight line joining the left edge and the point $(10k)$ where the rider is. And this equivalence holds for the slanting beam as well, and is independent of P. But the sensitivity of the beam with the rider on is evidently greater than it was with the rider off. Statically speaking, the weight of the beam and the two charges P and P are equivalent to a fixed point C_0 weighing $W'=W+2P$, and situated vertically below the axis of rotation at a distance S_0, and this particle, conjointly with the one embodied in the rider, is equivalent to a point weighing $W+2P+p$, and situated on the straight line between C_0 and the point where the rider sits. Referring to a system of rectangular co-ordinates whose X-axis passes through the centre of the central edge and is parallel to AB, and whose Y-axis passes through the same centre, we have for the position of the resultant point the equations

$$x(W'+p)=lkp \; ; \text{ and } y(W'+p)=W's_0-pH$$

$$\therefore \frac{x}{y}=tg\alpha=kp\left\{\frac{l}{W's_0-pH}\right\} \quad . \quad . \quad . \quad (4)$$

We see that if H be constant—*i.e.* if the rider-path be parallel to the plane of the three axes—$tg\alpha$ is proportional to the overweight kp virtually added to the charge of the right pan ; but it is as well to notice that the $tg\alpha$ of our equation is different from the $(tg\alpha)_0$ which is brought about if, instead of hanging the rider on the $(10k)$th mark, we actually put kp units into the right pan. Obviously

$$(tg\alpha)_0=(kp)\frac{l}{W's_0} \text{ and less than } tg\alpha \quad . \quad (5)$$

With a rider weighing only 10 milligrams, and, say, a hectogram balance, the term pH in the denominator comes to very little, but with a rider of ten times the weight it (as a rule) can no longer be neglected ; such a rider cannot conveniently be used unless H is constant and the rider must always hang at the balance (at its zero, over, say, the central knife when it is not used as a weight), or else the sensitivity has one value with the heavy rider on and another with the rider off. Another requisite is that notches cut into the beam be substituted for mere marks, and that the rider have a sharp edge to give sufficient constancy of position to its point of application.

From what we have said so far, it would appear that in a balance provided with a gravity-bob we can give the sensitivity any value we may fancy. And so we can, but it does not follow that we can command any desired degree of *precision*. Because the three edges and bearings are not what they ought to be, and, as a little reflection shows, the result of their defects is the same as if, say, the length of the right arm, instead of being at the constant value l, oscillated irregularly between $l-\lambda$ and $l+\lambda$, where λ is a very small length, which increases when W and P increase but is independent of l. And this again is the same as if λ were *nil*, but the charge of, say, the right side, instead of being at a constant value P, varied irregularly from $P-\epsilon$ to $P+\epsilon$. In a given balance charged with a given P at each side ϵ is constant, but the corresponding angle of deviation β varies when the sensitivity varies. Within this angle β the balance is, so to say, in a state of indifferent equilibrium. By going a little more deeply into the matter, we easily satisfy ourselves that, even allowing for the fact that we cannot substitute a longer for a shorter beam without increasing the beam-weight, ϵ will increase when l becomes less. In a balance meant to afford a certain degree of precision, we cannot allow the arm-length to fall below some (very uncertain) value of l_0.

A glance at eq. (2) would show, if it were not clear without it, that, if the three axes lie in exactly the same plane—*i.e.* if $h=0$—the sensitivity becomes independent of the charge, which is a great convenience. But h obviously cannot be equal to zero at all charges ; hence in the case of the best instruments it is regulated so that it has a small negative value when only the pans are suspended, and, by the unavoidable deflection of the beam, becomes zero at some suitably selected medium charge, so that, from this charge upwards, it has small positive values. That such a degree of precision cannot be attained by purely constructive methods goes without saying ; indeed, any precision balance requires to be "*adjusted*" before it is fit to be used. For this purpose the value of the h corresponding to the medium charge and the ratio of the actual arm-lengths $l':l''$ must be determined and the errors h and $\frac{l'}{l''}-1$ corrected. For the direct geometric measurement of h special apparatus have been constructed, which, in their present form, we believe, afford a sufficient degree of precision ; but the final test always is (or at least was until lately) at a suitable position of the bob, to determine the weight-value E^{-1} of one degree of deviation for a series of charges, say, $p=0$, 50, 100 g., etc., up to the maximum charge which the balance is intended to measure ; and to at least *virtually* calculate the corresponding values h by means of eq. (2). Whether h is positive or negative, is, of course, seen from the values E^{-1} without calculation. Supposing now h has a greater value than can be tolerated, one of the knives must be lowered or raised until at a certain medium charge the three edges are as exactly as possible in one plane. Most mechanicians provide adjusting screws for this purpose which enable one to work in a systematic manner. Some, however (for instance, Becker & Sons, following the example of Deleuil), prefer to fix all the knives definitely and to alter the *form of the beam itself* by means of the hammer. If the central edge has to be lowered, the lower bar of the beam is struck (on both sides) ; if it is to be raised, the upper bar is struck, until the correction is presumably almost but not quite completely effected. The values E^{-1} are then again determined, and if they are not sufficiently near one another, the hammering is renewed until the adjustment is perfect. In a similar manner (or by means of adjusting screws) the two arms are made equal to each other. The test here is very simple. The balance, after having been brought to the highest degree of sensitivity which it will stand at the highest charge P, is charged with *exactly* P grams on each side. The longer arm goes down, and by determining the small overweight which must be added to the other side to establish equilibrium, we can easily determine the ratio $l' : l''$ numerically. All these adjustments are effected by the mechanician, and when once effected are final. Some mechanicians—for instance, the Beckers—fix even the centre of gravity, but this is a mistake. A balance, to be complete, *must* have a movable " bob " to enable the operator to give the sensitivity that value which suits him best. What degree of sensitivity should we choose ? Answer : In general, the lowest degree which suffices for the purpose in hand. Supposing, for instance, we can neglect the half-milligram, it is of no use to screw up the bob any higher than necessary for rendering the angle of deviation corresponding to 0·5 milligram conveniently visible and no more, because the less the sensitivity, the greater the range of weights determinable by the method of vibration, the greater, as is easily shown from eq. (2), the relative independence of the sensitivity from the charge, and last, not least, the less the time of vibration. The time of vibration can, of course, not be allowed to fall below a certain minimum, or else the centres of gravity of the charges will not be able to follow the oscillations of the beam with sufficient promptitude. But this clause, with larger balances wrought at high precision, usually takes care of itself. The exact relation in a balance between the time of vibration t (in seconds) and the sensitivity E is given by equation :

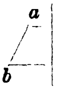
$$t^2 = \frac{l}{\mathrm{R1}}\left\{kW+2P\right\}\cdot E \quad . \quad . \quad . \quad (6)$$

where R is the length of the mathematical pendulum beating seconds at the place of observation, P the total charge on one side, and k a numerical factor, kWl^2 being the *momentum inertiæ* of the empty beam. With the customary perforated rhombus or triangle, k is very nearly equal to ⅓. From the equation we see clearly that with a " bob " of sufficient range we can choose our own time of vibration or our own sensitivity, but we cannot choose both, in a ready-made balance. It stands differently with a *balance to be constructed.* To avoid indefiniteness, let us assume that we wished to design a balance for weighing quantities up to 100 g. with a toleration of 0·1 mg. Let us assume also that we had made up our minds regarding the material and the general form for the beam, and that we had defined the latter so that the relation between arm-length l and weight W were in accordance with an equation of the form

$$W = C + Bl \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where W includes the empty pans, C designates the conjoint weight of all that which is independent of l ; and B stands for the weight of the rest if the arm-length $l = 1$. Our equation now assumes this form :

$$t^2 = \frac{l}{\mathrm{R1}}\left\{C^1+2p+bl\right\}E \quad . \quad . \quad . \quad (8)$$

where p stands for the charge in each pan. This equation affords some guidance in the selection of l. Assuming for E a value which renders the decimilligram just visible, and taking $p=0$, we substitute for t the smallest admissible value and solve our equation in regard to l. Of course, l cannot be allowed to fall below that minimum l_0 (*v. supra*) at which the inherent error would rise to anything like 0·1 mg. Where does this limit value l_0 lie ? Staudinger used to draw the line at 200, Oertling at 180 millimetres, and similar values were adopted by other makers, until Bunge showed in the most direct manner possible that a sufficient degree of constancy can be attained with an arm-length of as little as 60 millimetres. Thanks to the general excellence of Bunge's work his short beams soon became very popular with chemists, and the fact that almost all other German makers have since come to adopt the Bunge system shows that the additional perfection in the pivots which the short beam undoubtedly demands is not so difficult to realise as an outsider might be inclined to think. *Assuming this difficulty to be overcome,* it cannot be denied that the short in opposition to the long beam does offer certain advantages. First, it is relatively light, and hence the working of the arrestment is a less effort. Secondly, it is less liable to irregularities through one-sided elevation or depression of temperature. Perhaps we may add that, thirdly, it is easier in its case than in that of the long beam to make a smooth-working arrestment, and on this account chiefly it enables one to weigh more quickly. Fourthly, and *least* in our opinion, it vibrates more quickly. Not that we value this last advantage at nothing. The writer's auxiliary bob indeed was invented with the very object of remedying the corresponding defect in the older form of the instrument, being originally intended to be used thus. In the outset, place the bob far down, say to the mark where 1° of deviation corresponds to 2 mg. or some other value securing great rapidity of vibration, and establish equilibrium as far as thus possible. Then raise the bob to the mark at which 1°=0·1 mg., allow to vibrate, shift the rider correspondingly, and verify your result. The writer, however, soon came to find this method less convenient than he had expected, and adopted another very obvious expedient. It is easy in any beam to bring down the time of vibration to the least value one could reasonably wish for by screwing down the bob to the corresponding place. This, of course, may render the decimilligram deflection invisible to the naked eye. But why not help the eye by optical means? An ordinary lens magnifying six times linearly affords more than there is any occasion for; only it magnifies the parallactic error as well, and the effort to avoid this error strains the eye very unpleasantly. This experience led the writer to the following combination, which he found to give perfect satisfaction. A narrow ivory scale divided into degrees of about 0·1 mm. is fixed slantingly to the needle pretty far down, yet far enough up for not obscuring the ordinary scale which does duty as usual; on the other hand, a compound microscope of feeble power, which passes through the central fixed portion of the front pane of the case, is fixed slantingly to the *pillar*. The microscope has one vertical "wire" in its focus which acts as a needle. As the microscope inverts its images, the apparent motion of the wire in reference to the scale (which one easily persuades oneself is fixed) is the same in sense as the real motion of the needle in reference to the ordinary scale, so that mistakes in regard to the + and − are avoided. The ordinary scale is graduated after the micro-scale so that each of its degrees is equal in angular value to 10° of the latter. The writer some five years ago caused Mr. Oertling to apply this arrangement to two of his balances, and he has found it to work very satisfactorily. Although it was originally intended chiefly for special occasions—the adjusting of weights, etc.—it is used even for our everyday work, as it was found that the microscope puts a less strain on the eye than the naked-eye reading of the ordinary scale. The microscopic arrangement described adds about £3 to the cost of the balance. A cheaper arrangement is the following. A micro-scale, divided conveniently into fifth-millimetres, is fixed slantingly to the pillar, the needle at the corresponding part is shaped thus, 

and a hair by means of capillary perforations is stretched out between *a* and *b*; the hair is parallel to the face of the scale, and only some 0·2 to 0·5 mm. removed from it. A short terrestrial telescope, fixed in the central (fixed) part of the front-pane of the case, serves for the readings. The object glass serves only to produce an image of the scale and hair within the tube, which the eye-piece (a compound microscope) magnifies as far as necessary. As the telescope need not be perfectly steady, it can be fixed at a relatively low cost. We have used this arrangement in connection with one of our balances for over two years, and found it to be almost as good as the one first described.

On the Setting up and Testing of a Precision Balance.

A real precision balance, to be able to do justice to itself, must stand on a very steady support, in a room where it is not exposed to one-sided changes of temperature. The light should fall in from the back of the observer. The best support, of course, is a pillar of masonry, standing directly on the earth. Next after it (in a substantially built building) comes a shelf fixed to the wall by strong brackets. A good heavy table, however, suffices in practice. In a large city the street traffic becomes very inconvenient in weighing. Its effect can be minimised by putting small pieces of thick vulcanised-rubber plate between the legs of the case and the table. In the examination of a newly set-up balance we naturally begin by seeing that the arrestment, the rider-shifting apparatus, etc., are in good order, we then level the case, and next leave the balance to itself for some four hours at least, to enable it to acquire the temperature of the room. After these preliminaries we proceed to the following determinations.

Determination of the inherent error ϵ.—For this purpose we charge the balance equally on both sides with the highest weight which it is intended to measure (a hectogram balance, for instance, with a hundred-gram piece on each side), and after having established approximate equilibrium at the highest degree of sensitivity which the balance will stand at this charge without giving obviously inconstant readings, determine the exact position of rest, first with the two hectograms in the centres of their pans, and then, in a series of successive experiments, with one or other of the hectograms placed at some point of the edge of its pan so as to give any non-parallelism in the axes or any other defect in the terminal pivots a good chance of influencing the result, taking care to interpolate occasionally an experiment with the two weights centrally placed in order to see if the balance still gives the same readings as it did at first. If it does not, this is probably owing to external causes, such as unequal heating of the two arms. To be able to translate degrees of deviation into differences of weight, we must at some stage make two successive determinations of the position of rest, one with P' in the left and P'' in the right pan (P' and P'' stand for the two hectogram-pieces), and another with, say, one milligram added to P''. For the precise determination of a position of rest, we cause the balance to vibrate moderately, and (neglecting the first few readings as being in general liable to irregularities) record 3, 5, 7 . . . successive turning-points of the needle; those on the left, as seen through a telescope, are termed positive and marked +, whilst those on the right are regarded as negative and marked −; an odd number in any case in order to correct for the retarding effect of the resistance of the air, etc.; those influences, in other words, through which the needle, supposing it to start from $-4°$, at the end of a double vibration, does not come back to exactly $-4°$, but perhaps to $-3·7°$. The algebraic sum of any two successive readings gives the point a of the scale at which the needle would come to rest, *in half-degrees*, and there is no reason why the half-degree should not be adopted as a convenient unit for the purpose in hand. Supposing the readings to be:

$$\begin{array}{llllll} & a_1 & a_2 & a_3 & a_4 & a_5 \\ \text{(Example)} & +3·7 & -2·7 & +3·5 & -2·4 & +3·5 \end{array}$$

we have for a the values: $a_1+a_2=+1·0$; $a_2+a_3=+0·8$; $a_3+a_4=+1·1$; $a_4+a_5=+1·1$—Mean $=+1·0$.

The mean value of the four results is put down as *the* value of a. Supposing a, through the addition of $\triangle$ milligrams to the right charge, to increase by n demi-degrees, then $E=\frac{n}{\triangle}$ ($=2$ "E" in the sense of our equation (2)) is the sensibility in demi-degrees; and its reciprocal $E^{-1}=\frac{\triangle}{n}\left(=\frac{1}{2E}\ldots \text{of equation (2)}\right)$ the weight-value of the demi-degree in milligrams. Supposing the values for a obtained with abnormal positions of the charges to be a_1, a_2, a_3, etc., instead of the mean value a_0, corresponding to the centrally placed charges, then $(a_0-a_1)E^{-1}=v_1$, $(a_0-a_2)E^{-1}=v_2$, etc., give each a value for the *inconstancy* of the balance in milligrams (or rather fractions of a milligram, it is to be hoped). According to a rule deduced from the law of frequency of error, the computation:

$$r=\frac{0·845}{\sqrt{n(n-1)}}(v_1+v_2+v_3+\ \ldots\ .)$$

where all the v's must be taken as positive, gives the "probable" weight-value of the deviation of any one a from a_0, meaning that value of $(a_0-a)E^{-1}$ which, in a *very large number* of determinations, is as often exceeded as not reached. But in practice the number of determinations made is never sufficiently great to bring out anything like a close approximation to the law, and it suffices to take r as being equal to 0·845 times the mean of all the values v, and adopt it as sufficiently near to the theoretical "ϵ." The probability that, in a given case, $(a_0-a)E^{-1}$ *exceeds*

$$\begin{array}{lllll} & 2r & 3r & 4r & 5r \\ \text{is} & 0·18 & 0·04 & 0·007 & 0·0007 \end{array}$$

respectively.

In these determinations, if the balance lacks a microscopic reading arrangement, it is as well to read from a distance with a telescope, to avoid the parallactic error which we have no right to charge against the balance.

Determination of h.—All that is necessary is to determine the weight value of one degree in the sense of equation (2) for, say, $p=100$, 75, 50, 25, 0 g., and to calculate the corresponding values h. In a good balance h is so small that (supposing our rule regarding the adjustment of the bob to be followed) the sensitivity remains almost constant from $p=0$ to $p=100$ g. Hence, practically, it suffices to adjust the bob so that at a convenient average charge (where "average" refers to the most frequently occurring values of p) one demi-degree corresponds to, say, ½ or ⅓ of a milligram *exactly*, and then to see what it is at other charges. If there is no sufficient constancy we enter the values E^{-1} found on a system of rectangular co-ordinates in function of the charges p, and draw the nearest curve to the points. This curve (if h were absolutely constant) would be a straight line. In any case it supplies the data for a table of values for E^{-1}. This table, however, must not be relied on in *standard* weighings, because the value h is subject to changes, for this reason amongst others, that the agate of the knives has a different coefficient of expansion from the metal of the beam.

The *arm-lengths.*—For the determination of the ratio of the arm-lengths, the orthodox method (for a hectogram balance) is to adjust two hectogram-pieces to exact equality, and, after having established equilibrium, to put one into the left and the other into the right pan, etc. But in practice the following method is better. Take any two fairly well adjusted hectograms and viewing them, one as a *standard* representing 100,000, the other as an *object* weighing x milligrams, go through the ordinary operation of weighing once with the object in the left pan and the standard in the right, and once the other way.

Supposing (using S as a symbol for 100,000 milligrams) we find

$$xl'=(S+\delta_1)l'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I}$$
$$xl''=(S+\delta_2)l' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{II}$$

(where any δ may be negative), we have by division of I by II, and subsequent multiplication with $l'':l'$,

$$\left(\frac{l'}{l''}\right)^2=\frac{S+\delta_1}{S+\delta_2}=\frac{1+\frac{\delta_1}{S}}{1+\frac{\delta_2}{S}}$$

whence, as a sufficient approximation,

$$\frac{l'}{l''}=1+\tfrac{1}{2}\left(\frac{\delta_1-\delta_2}{S}\right)$$

No maker who has a name to lose would care to send out a precision balance in which $1-\frac{l''}{l'}$ is more than $\pm 0·00005$ at the outside, although for any scientific purpose a considerably greater error could be tolerated. The corresponding adjustment indeed, while of the first importance in commercial balances, in precision balances is in a sense irrelevant.

Bibliography.—(1) *Leonhard Euler*: "First Development of the Theory of the Balance," Trans. of the Petersburg Academy.

(2) *Wilhelm Weber*: Balance: Göttingen gelehrte Anzeigen for 1837, 287. Description and Drawing in Carl's Reportorium für physikalische Technik, 1, 18.

(3) *Löwenherz*: Report on Metrological Instruments in Bericht uber die wissenschaftlichen Apparate auf der Londoner Ausstellung in 1876; Braunschweig, 1881. Vacuum Balances, 223–232. Balance Beams, 232–237. The

Pivots : Modes of Fixing the Knives, 237–245 ; Bearings, 246–247 ; Arrestments, 248–253.

(4) *Löwenherz* : Zeitschrift für Instrumentenkunde for 1881, 125 ; Report on Sartorius' Hinged Arrestment Frame.

(5) *Löwenherz* : same Journal, year 1881, 184. A Report on Apparatus for Measuring Small Weights by the Torsion of Wires: Hooke, Ritchie, Sartorius. Full drawing of Sartorius' contrivance on p. 188.

(6) *Dittmar* : Waage des Chemikers ; same Journal, year 1881, 313–326.

(7) *Dittmar* : same Journal, year 1882, 63 ; Mikroscopische Ablesungsvorrichtung für feine Waagen.

(8) *Dittmar* : R. Soc. Ed. Proc. for 1876 ; Chem. News, 33, 157.

W. D.

ON HIGHLY ACCURATE WEIGHING.

Introductory.—In the late Professor Dittmar's article (*vide supra*), typical precision balances have been considered ; the theory of the balance and the conditions necessary for accurate work in general have also been duly treated. We therefore confine ourselves to a description and consideration of certain exceptional precautionary measures indispensable for the attainment of the highest degree of precision in weighing.

This article is based chiefly upon results obtained during two researches which, for successful issue, demanded more than usual care. The subject was of necessity studied from the severely practical point of view ; and few, if any, of the remarks that follow have their foundation in pure theory alone. The following matters are severally discussed :

(1) The Balance Room.
(2) The Balance Table.
(3) The Levelling Screws.
(4) The Scale.
(5) The Illumination of the Scale.
(6) Of possible Variations in the Level of the Bench.
(7) The Telescope and its Carriage.
(8) Of the Necessity for Fatiguing the Beam.
(9) Device for Maintaining Uniformity in the Temperature of the Beam.
(10) Temperature Coefficients of a Balance.
(11) Suppression of Air-Streams about the Pans.
(12) Concerning Ordinary Balance Cases.
(13) Optical System.
(14) A New Device for Riders.
(15) Invar Steel Balances.
(16) Aperiodic Balances.
(17) Micro-balances.
(18) Chainomatic Balances.
(19) Concerning the Wiping of Glass Vessels.
(20) Precautions taken in Weighing Glass Vessels.
(21) Apparent Change in the Weight of a Cooling Body.
(22) Of the Different Methods of Weighing.

(1) *The Balance Room.*—The balance room should be in the basement ; and in selecting it, the choice should fall upon one having a north-easterly aspect : for then comparatively little direct sunlight can enter the window even during midsummer. A dry, airy cellar is an almost ideal room for a balance that is to be used for highly refined weighing. But in either case, and particularly so in the latter, the variations in the temperature of the air within assume minimum values ; this is frequently of great import. For a series of weighings, no weather is so favourable as that which prevails when the sky is overcast and wind absent.

(2) *The Balance Table.*—For work of supreme accuracy, it is imperative that the balance be placed upon a massive pillar of brickwork or stone ; and this should rest upon a foundation sufficiently deep to guard against all local vibrations. The flooring should not have direct contact with the pillar ; otherwise vibrations may readily pass from the former to the latter, and so to the balance. An excellent plan is to cap the pillar with a rectangular block of slate : this may have a thickness of from 1 to 1·5 inch. The slate should be closely cemented to the main block, and have its upper surface as far as possible truly plane. The slate, freed from all grit and dust, is covered either with a single fold of white linen or with white blotting-paper ; and upon this is placed a sheet of thick plate glass, some 2 or 3 inches shorter and narrower than the slate. The paper or linen serves a twofold purpose : first, it acts as a necessary and convenient pad between the glass and slate ; and, secondly, it secures for the worker a permanently white surface which renders even small objects sufficiently conspicuous. Near each corner two holes are drilled in the slate, for the reception of wooden pins having rubber-covered heads. The positions of these are indicated in Fig. 6.

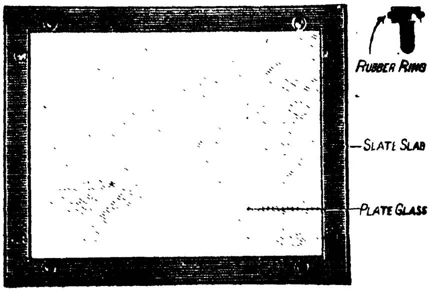


FIG. 6.

The pins guard against any accidental displacement of the glass.

(3) *The Levelling Screws.*—With the above-described bench we may with advantage dispense with the brass shoes commonly employed for the levelling screws. When this course is adopted, the screws at their lower ends should terminate in highly polished spherical surfaces of low curvature. At those points where the screws have contact with the glass, a little oil is applied ; medicinal paraffin oil is, on account of its non-liability to thicken, admirably suited for the purpose. The base of a balance thus mounted readily adapts itself to modified conditions resulting from changes in temperature ;

and inherent stresses and strains are very little if at all affected.

(4) *The Scale.*—In some balances the scale divisions have an excessive length and breadth. Long lines produce an apparent narrowing of the contained spaces ; and this increases the difficulty, already sufficiently great, of correctly estimating the turning position of the pointer. Again, a broad line is in general a very considerable fraction of a division ; it is not easy to allow for this, and possibly the matter is sometimes overlooked. These two imperfections are reduced to insignificant proportions as follows.

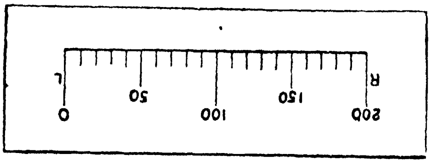


Fig. 7.

The slip of ivory is detached from the pillar, and the scale completely removed by lightly rubbing the ivory upon a very fine, large flat file ; the slip is then re-polished, and a new scale in millimetres engraved upon it. The engraving tool must be capable of producing the finest of lines, and these are lightly drawn. The divisions, which may have a length of 1 mm., are rendered distinct by the momentary application of an etching pen charged with Indian ink. The ink readily runs along the whole line ; occasionally a line may appear a little irregular ; but after the ink has dried, any unevenness may be remedied by gently re-polishing with a flat pad. Fine sharp lines may often be secured by a *partial* filing down of the original scale, and the requisite shortness by a *complete* removal of the lower portions of the lines. During the process of shortening a straight-edge is used, not only as a guide for the file, but also as a protector for the portion of the scale to be retained.

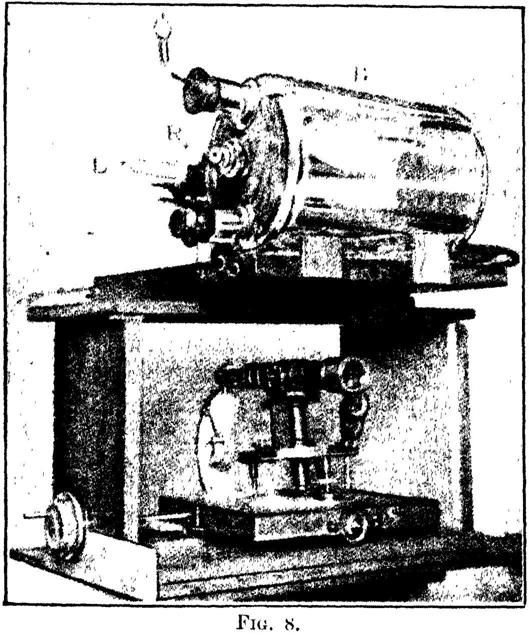


Fig. 8.

As the scale is invariably viewed through a telescope, which inverts the divisions and reverses their order, additional convenience is gained and possible confusion avoided by numbering principal lines as shown in Fig. 7.

(5) *The Illumination of the Scale.*—Weighings should be carried out in the absence of daylight ; for unless the light from the window falls upon the balance in a perfectly symmetrical manner, and in general it is difficult to ensure this, the radiant energy absorbed by one part of the instrument will differ in quantity from that absorbed by another ; this in itself would be immaterial, provided the ratios of the several quantities remained constant ; but direct experimental evidence reveals fluctuations in these, and therefore corresponding variations in the zero or resting-point, R.P., of the beam follow. By using artificial light, we can eliminate this particular source of error. The following device leaves little to be desired :

A Woulf's bottle B, Fig. 8, having a volume of 15 litres and filled with a solution of potassium dichromate, is placed horizontally upon a shelf above the reading-telescope. A long tubular glow-lamp L, carried by a stand R, is set up parallel to and behind the bottle, and the position of the lamp so adjusted that a bright band of light illuminates the beam of the balance. The charged bottle forms not only a cylindrical but also a heat-absorbing lens ; and, owing to the monochromatic nature of the light, the lines of the scale are seen sharply defined. The pointer and its scale are similarly illuminated by raising the lamp.

(6) *Of Possible Variations in the Level of the Bench.*—An error which is readily overlooked is that originating in variations in the level of the balance table. Observable changes may quickly follow a *sudden* rise or fall in the temperature of the room. Usually of a transitory nature, they are at times particularly noticeable and definite in a bench supported by wall brackets fixed above hot-water pipes. The variations are probably due to minute deformations resulting from inequalities of temperature. In connection with refined weighing, it is obvious that some plan must be adopted for detecting and measuring such variations. We have used with success the following simple form of tiltometer.

At one end of a glass tube T, Fig. 9, having a diameter of 3 cm., and a length of some 3 or 5 cm. greater than that of the balance pointer, a short capillary is formed; the other end is ground so that its containing plane is at right angles to the axis of the tube. Next, a short piece of platinum wire W_1, having a diameter of 0·5 mm., is, by means of gold, joined to one end of another platinum wire W_2, having a diameter of 0·05 mm., and a length some 3 cm. less than that of the tube; the free end of the fine wire is attached to a small cylindrical weight Y which keeps the wire taut; the resultant plumb-line is then introduced into the tube and the thicker wire fused into the capillary at the top. Any error in centring is remedied by a suitable bending of the wire W_1. A short scale, S, mounted upon a half-cylinder of boxwood, is fixed within the tube, so that its distance from the point of suspension of the fine wire equals the length of the balance pointer. The scale consists of 5 very small dots instead of lines; and the spaces they mark off are equal to the corresponding spaces of the scale behind the pointer; they are with advantage numbered and lettered according to the plan shown in Fig. 7. Vibrations of the plumb-line resulting from a necessary or accidental disturbance of the instrument are quickly damped by oil in the vessel V. The tiltometer is completed by mounting the tube upon a rectangular base of thick plate glass, the width of which is somewhat less than that of the balance case, and its length some 3 or 4 inches greater. To the lower surface of the base are attached, by means of Canada balsam, 3 steel balls, *b*, *b*, *b*, and these are so disposed that when the instrument is *in situ*, each ball is in close proximity to a levelling screw *a* of the balance. The position occupied by the tiltometer relatively to that of the balance is shown in Fig. 10. When correctly adjusted, the scale of the instrument and that of the balance pointer at C are in one and the same horizontal line, and they are contained by a vertical plane common to both.

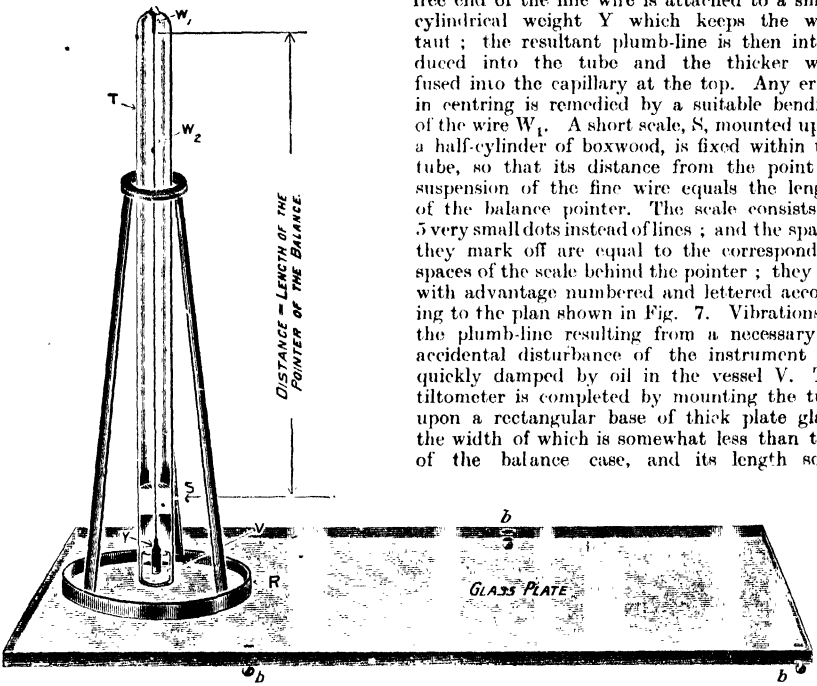


FIG. 9.

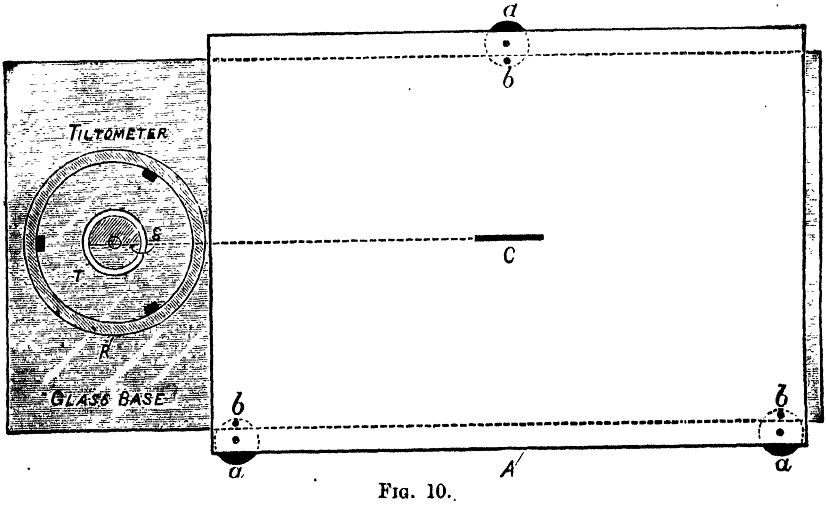


FIG. 10.

With the tiltometer placed as indicated, it is evident that any vertical movements of the levelling screws resulting from a flexure of the bench are also imparted, and in the same degree, to the tiltometer. Such movements, provided they are strictly equal, are not detrimental, and they pass undetected ; but unequal flexures effect a change in level. Any appreciable differential changes taking place along a line joining the two ends of the balance case are detected and may be measured by the tiltometer.

The tiltometer tube is protected by surrounding it with a metal guard, the base of which is a heavy brass ring R ; this ring is prevented from being easily moved by smearing its under surface with resin cerate. The tube and its guard have no direct contact. For a series of weighings we proceed as follows.

The telescope (Fig. 8) is first brought opposite the tiltometer and the position of the plumb-line determined with the aid of the micrometer. Next, the telescope is moved along until the scale behind the pointer appears in the field of view ; the weighing is then carried out with all due precautions. Lastly, the tiltometer is re-observed : if the former and latter readings are identical, and they rarely differ within so short a time, the data for the weighing may be accepted ; otherwise the experiment is rejected and a new one undertaken. When carrying out a new weighing at a later hour or on another day, the tiltometer reading may be slightly larger or smaller ; but given an accurate knowledge of any such difference δ, the new weighing is easily reduced and made strictly comparable with the first by the addition of $+\delta$ to the second value obtained for the resting point R.P., of the beam.

(7) *The Telescope and its Carriage.*– For observing the vibrations of the pointer, the best and most convenient plan is probably that in which the telescope is mounted upon a firm bench at a distance of some 2 or 3 metres from the balance. In order that the pointer as well as the tiltometer may be readily and successively viewed, the telescope is placed upon a carriage having for its guide a V-groove set at right angles to the line of vision. The carriage has three supports ; two consist of brass balls, which rest in the groove; the third support is a broad wheel of boxwood. Easy and smooth movement is ensured by lubricating the groove with tallow. In order that the tiltometer (*v. supra*) may be read with accuracy, the eyepiece of the telescope is fitted with a horizontal micrometer M, graduated to 0·01 mm.

(8) *Of the Necessity for Fatiguing the Beam.*—Although from the practical point of view a balance beam may in itself be perfectly inflexible, it is as yet impossible so to incorporate the knife-edges that they and the beam shall constitute one absolutely rigid whole. On releasing a loaded beam, the consequent stresses bring about slight relative movements of the several knife-edges and their screws. Such movements frequently affect, although in minute degree only, the ratio of the lengths of the balance arms. The time required for their completion varies not only with the balance, but also with the load, and it may range from few to many minutes ; but, in general, a period of from 10 to 15 minutes suffices. Now, from the above, it will be evident that no weighing can be of definite value unless the knife-edges have already assumed truly normal positions ; and in order that they may do so, the balance must be *fatigued.* This simple operation consists in allowing the beam to vibrate, for an appropriate time, after the pans have been loaded and the weights adjusted for weighing ; the beam is perfectly fatigued when successive R.P. determinations agree. Having reduced the balance to a normal state, the actual weighing is undertaken ; and for this the crank handle is first cautiously turned, so that without in any way relieving the instrument of its load, one of the arrestors is momentarily and very gently made to lift its pan and thus cause the beam to re-oscillate. Several vibrations having passed unrecorded, the usual observations for the determination of the R.P. are carried out. The above remarks concerning fatiguing are equally applicable in the case of an " unloaded " balance. In Fig. 11 we have an illustration typical in character and magnitude of initial knife-edge movements. The curve there shown, and in which successive R.Ps. are graphed against corresponding time intervals, represents the results of an experiment with a highly inflexible beam of the cantilever form. The movements, at first of an oscillatory nature, die away and finally the R.P. acquires a constant value.

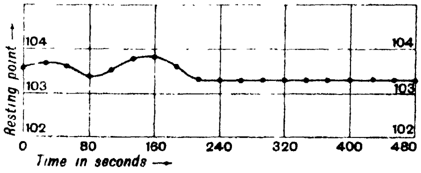


FIG. 11.

If for any reason the loaded beam is arrested, the balance must again be fatigued before proceeding with a final weighing. When it is necessary to readjust the position of the rider upon the fatigued beam, the operation may be carried out without detriment, by first slowly raising the pan arrestors until they are in such a position that, although they do not support the loaded pans and so relieve the beam, they reduce the vibrations to a very small amplitude.

(9) *Device for maintaining Uniformity in the Temperature of the Beam.*—If a differential bolometer is arranged within a balance case, so that its two resistance coils are separated by a distance equal, say, to the length of the beam, it is easy to show that small and rapid fluctuations in the temperature of the air are continually taking place, even when the case is closed. On lifting the shutter the fluctuations become more marked, and during the loading of the pans they are, comparatively speaking, quite violent. A pair of sensitive mercury-in-glass thermometers similarly placed naturally fail, on account of their sluggishness, to indicate variations in temperature ; they show a mean

value only. In order that the highest degree of precision may be attained, it is imperative that the temperature of the air enveloping the beam should remain strictly uniform for at least some time, both before and during the process of weighing. This uniformity may be ensured by the device illustrated in Fig. 12, which depicts in addition to the usual balance case, a small inner auxiliary chamber which completely encloses the beam. The base plate *c*, *d* of this chamber is of aluminium, having a thickness of 2 mm. or more ; it is suitably slotted and perforated for the passage of the pointer and hooks by which the pans are suspended. The ends E, F are conveniently made of well-seasoned mahogany, having a thickness of 1 cm. The front, back, and also the top of the chamber are of 8–10 mm. thick plate glass. The front of the chamber may be removed and the beam thus rendered accessible, after dropping the holders *h*, *k*. Discs *r*, *s*, *t* of thin aluminium are fastened to the pointer and pan hooks a little below the base plate ; these screen the apertures immediately above them. When placed within the auxiliary chamber, a differential bolometer recording variations as small as $\frac{1}{5000}$°C. remains quite unaffected, even during the loading of the pans. The decided advantage held by the protected over the unprotected beam is very well shown in Fig. 13. The groups *a*, *b* are the bolometer records obtained when, using nine weights, one of the pans was loaded and unloaded six times in succession. During the experiments the position of the bolometer near the beam remained unchanged.[1]

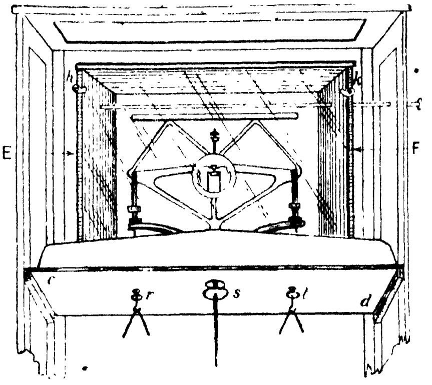


Fig. 12.

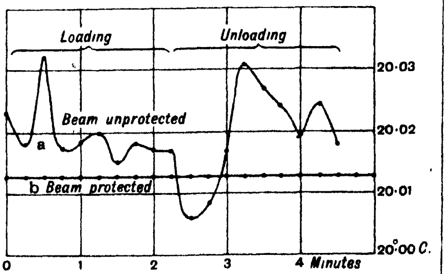


Fig. 13.

(10) *Temperature Coefficients of a Balance.*—Other conditions being constant, the R.P. of a beam will, in general, vary simultaneously with the temperature ; therefore, unless the balance is thermostatically controlled, we must know with considerable exactitude the *temperature coefficient k* of the instrument. The value of *k* will vary with the balance and also with its load ; but for a given balance, the several values of *k* for different loads may be determined as follows :

Commencing at an early hour, when presumably the temperature of the room is at its lowest, and with the pans as the only load, the beam is released and duly fatigued ; the R.P. is then found and the thermometer in close proximity to the beam read. Using hot-water pipes, an electric radiator, or a gas-fire, the temperature of the room is next raised by about 2°C. ; a little later the R.P. is redetermined and the thermometer within the balance case read a second time. Proceeding in this way step by step, a total range of temperature of some 10° or 12°C. is covered. Finally, the room is allowed to reassume its original temperature, or approximately so, and a last determination of the R.P. for this series made. If the first and last members of the series are in agreement, the R.P. values for the higher temperatures should be reliable. From the data thus obtained, a temperature coefficient curve is now prepared by plotting the R.P. values against those for the corresponding temperatures ; the resultant graph enables us to discover the true R.P. for any temperature falling within the experimental limits and for the particular load employed. (In this case, the so-called zero load.) Extrapolation should never be resorted to ; for *k* may at any other temperature assume a distinctly different value ; its sign may even be reversed : and so *k* from being an additive may become a subtractive quantity. Usually it will be sufficient if the temperature of the beam is known to 0·05°C. The thermometer is placed horizontally within the auxiliary case.

With the completion of the above, further operations identical in kind are proceeded with ; and unless the balance develops abnormal behaviour, experiments with four additional loads will suffice. For a 200-g. balance the several loads may conveniently be 50, 100, 150, and 200 g. The results obtained with each of these loads are, as before, represented by smoothed graphs, all drawn upon one and the same sheet. Often these graphs are of the same family ; with such a group we may, for the given range of temperature, make use of interpolated values for drawing the temperature coefficient curve corresponding to an intermediate load. Finally, the whole series is completed by a redetermination of the R.Ps. for the unloaded pans : the value of all the results is thereby greatly enhanced.

---

[1] An excellent plan is to permanently set up a differential bolometer in the immediate vicinity of the beam ; the thermometric condition of the enveloping air can then be readily tested at any time.

Characteristic curves for *k* for a 200-g. balance are reproduced in Fig. 14. The two dotted line curves were derived from interpolated values.

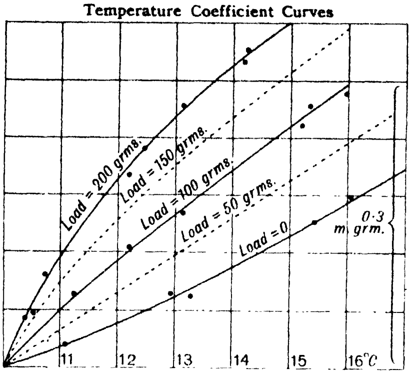


FIG. 14.

(11) *The Suppression of Air-streams about the Pans.*—Increased accuracy is secured and labour saved by adopting some plan whereby uniformity in the temperature of the air surrounding the pans is ensured; one that in practice has proved highly efficient is illustrated in Fig. 15.

Each pan, together with its stirrup, is enclosed by a fixed and massive brass cylinder C, having a diameter but little greater than that of the pan. The cylinders extend from the floor of the balance case, where they fit into grooves in thick brass plates P, P, to the aluminium plate of the auxiliary chamber above; and each is surrounded by a slightly larger cylinder B, which rests upon 3 wheels attached to C; these wheels, of which four lettered W are shown, are placed apart at an angle of 120°. By covering that portion of the fixed cylinder enclosed by B with silk, a smooth and easy movement is imparted to the latter when the handle H is pressed towards the right or left. To render the pans accessible, large rectangular apertures A are cut in the cylinders C, C; these are opened or closed by appropriate rotations of B, B. In the figure the left-hand cylinder is open and the other closed. The interior surfaces of the cylinders are coated with a dead-black lacquer, but the exterior surfaces are polished and left unvarnished. Now, theory and practice alike show that with these conditions, a temperature uniform in the highest degree, and one, moreover, unsusceptible to any but slow variations, is quickly established. But given uniformity in temperature, it follows that within a space so limited and confined winds or air-streams are non-existent; and therefore the minor irregularities ordinarily arising from convection currents about the pans are avoided.

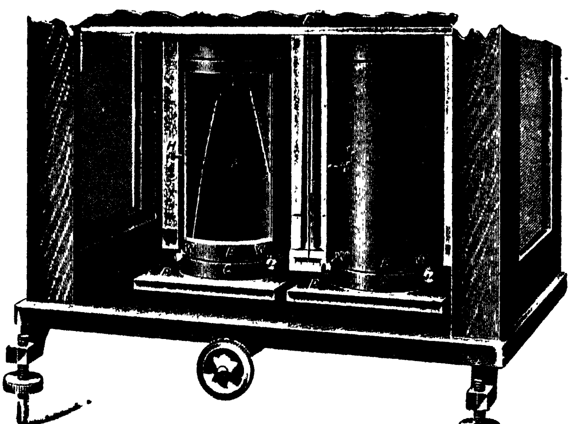


FIG. 15.

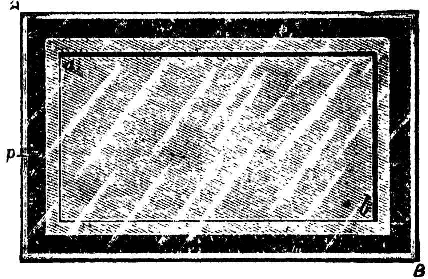


FIG. 16.

(12) *Concerning Ordinary Balance Cases.*—(*a*) With few exceptions the top of the usual balance case consists of a sunk glass panel *a*, *b* (Fig. 16); this is a constructional defect which we remedy in the following way. A strip of velvet *p* about an inch wide is fastened by means of thin glue or seccotine along the four sides and near the edges of the top of the balance case, as shown in the accompanying Fig. 16.

When the glue has hardened, but not before, a piece of plate glass AB sufficiently large to just overlap the rectangle is placed upon the velvet. The velvet surface not only grips the glass and thus prevents it from being readily disturbed, but also acts as a highly efficient filter and so prevents dust from penetrating to the ordinary panel within. The added panel is easily dusted, and during the cleaning we do not as before incur the risk of forcing dust between the glass and the supporting surfaces and so to the interior of the balance case.

(*b*) The case of a precision balance should be opened or closed by sliding rather than by hinged doors. When a hinged door is opened the pressure of the air within the case is momentarily lowered; in consequence of this, the external air rushes through the innumerable crevices in the framework, and sweeping before it the erstwhile quiescent dust, charges the space within with floating particles. This fact may be verified by conducting an experiment in bright sunlight; on opening the door the sunbeams at once reveal the incoming dust.

(*c*) All sliding doors should run with great smoothness, and they should be fitted with counterpoising weights after the manner of ordinary window sashes. Shutters that are arrested by clutches are highly objectionable. During the working of a clutch vibrations are set up, and these are communicated to the balance with detrimental effects. Two other devices which materially assist the metrologist are (i) an optical system for measuring the vibrations of the beam, and (ii) arrangements for the use of two riders. These we now briefly describe.

(13) *Optical system.*—Optical devices for determining the R.P. are now to be found in various precision balances. That used in conjunction with our own instrument was set up in the following way.

The central knife-edge block was drilled and one end of a fine aluminium tube inserted and secured. Into the other end of the tube, which was centred in a small opening in the front panel of the beam case shown in Fig. 12, was thrust a wire supporting an optically flat palladium mirror. The mirror, adjusted vertically, faced a miniature window of parallel-plane glass situated in one end of the balance case. Multiple images were avoided by setting the window slantwise. Opposite the window, and at a distance of 1·5 metres from it, was placed a brightly illuminated and perpendicular millimetre scale. For sighting the image of this scale, use was made of a reading-telescope adjusted to view the mirror, and fixed at a distance therefrom of 4·5 metres; thus the effective length of the pointer of light was 9 metres. The length of the ordinary pointer of the balance was 30 cm. only; therefore the precision with which deflections of the beam were now determinable had been increased thirty-fold. It will be obvious that the accuracy here attained could have been surpassed by the simple expedient of removing the telescope to a greater distance.

(14) *A New Device for Riders.*—The scale for the rider is engraved upon the beam or upon an attached thin strip of metal. The upper surface of the beam is either flat or bevelled. A bevelled beam may be graduated or serrated. In the case of the flat top, the position of the rider is indicated by a scale cut upon the face of the beam; and this plan is for most purposes sufficiently accurate. It is, however, assumed that the crown of the placed rider is equivalent to a horizontal right line running strictly perpendicular to the length of the beam. But, in general, the crown is neither perfectly straight nor placed with theoretical accuracy. Errors arising from these two defects are greater for a beam that is flat than for one which is serrated. In the case of the latter they become, provided the bevel is acute and the serrations shallow and geometrically correct, vanishingly small. But when a series of rider settings is carried out with a beam which is not bevelled it is found that successive R.P. determinations differ very appreciably. For increased accuracy the rider may under these circumstances be adjusted several times and the corresponding R.Ps. measured. From the values so obtained, a mean is then calculated and accepted as the best available.

Another source of error may arise from an inaccurate spacing of the scale divisions or the serrations as the case may be. In illustration of this we quote the results obtained by calibrating two high-grade beams by means of micrometer microscopes. One beam was flat and the other serrated. In the first case the extreme difference in the spacing was 8·2%, and in the second 0·8%. Expressed as possible variations in weight, the respective errors were 0·085 and 0·008 mg. Such errors were in our own balance minimised as follows.

To each end of the beam and at the back of it was attached by means of screws an L-shaped plate of aluminium, as shown in Fig. 17. Two riders, having the form shown in *b*, Fig. 17, were made and their flat portions perforated. One rider was of gold and the other of aluminium; the first weighed 10 mg. and the second 1 mg. After the riders had been duly adjusted, a platinum wire 0·1 mm. in diameter was drawn through each; the two wires were then passed though holes pierced in the L-shaped plates, drawn taut, and secured as depicted (Fig. 17).

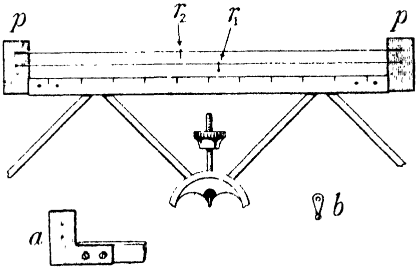


Fig. 17.

The addition of the new rider apparatus rendered the beam unstable. The defect was remedied by dividing the gravity bob into two. One-half was retained in its original position, whilst the other was attached to the uppermost part of the pointer rod, which was threaded for its reception. Thus the beam now had two gravity bobs, one above and the other below the central knife-edge; and by these the beam was re-stabilised and the required sensitivity imparted.

For moving the riders a new apparatus was constructed. An end-on view of this is given in Fig. 18. In the figure, A is a stout brass plate drilled for the reception of the operating rod; w_1 and w_2 are two platinum wires 0·2 mm. thick, fixed and bent as shown. The relative positions of the riders r_1 and r_2 upon their wires are also indicated. The movements of the stops s_1 and s_2, about the centre *c*, are limited by a glass surface *f*, *g*. This limitation guards the stretched wires against undue pressure from w_1 and w_2. By suitable horizontal and rotational movements of the plate A, the wires w_1 and w_2 can be brought to bear against either face of the corresponding rider ; and then by pushing or pulling as may be required, the rider can be moved to any point of the supporting wire.

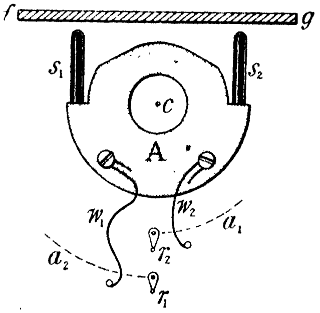


FIG. 18.

Having completed these new arrangements, it was then impossible to define with precision the positions of the riders. A further duty was therefore imposed upon the mounted telescope of Fig. 8, and weighings conducted as follows.

First the pans are loaded and the two riders appropriately placed. Next, the loads having been almost exactly equalised, the R.P. is determined under the conditions already detailed and the beam arrested. Finally, by means of the tilting screw *n* (clearly shown in Fig. 19), the telescope is directed to view the beam scale, and then moved along its platform until its fine vertical cross-thread covers the thin edge of one of the two riders, the position of which is read by means of the scale. The position of the second rider is similarly determined.

It will be seen that the position of the riders are in this way ascertained only with the usual degree of precision.

But even so, two distinct advantages are gained. In the first place the riders cannot be dropped ; hence, possible loss and damage are eliminated. Secondly, the position of each rider is precisely defined, and its seat upon the supporting wire is as it should be, equivalent to a fine line drawn at right angles to the plane of the beam. A more accurate determination of the position of either rider was rendered possible by the following plan.

In Fig. 19 is shown a tangent screw *t* by which the telescope may be turned through a small angle about its vertical axis. The screw possesses a large head *k* ; also an index *i* which can traverse an arc *a*, graduated in millimetres.

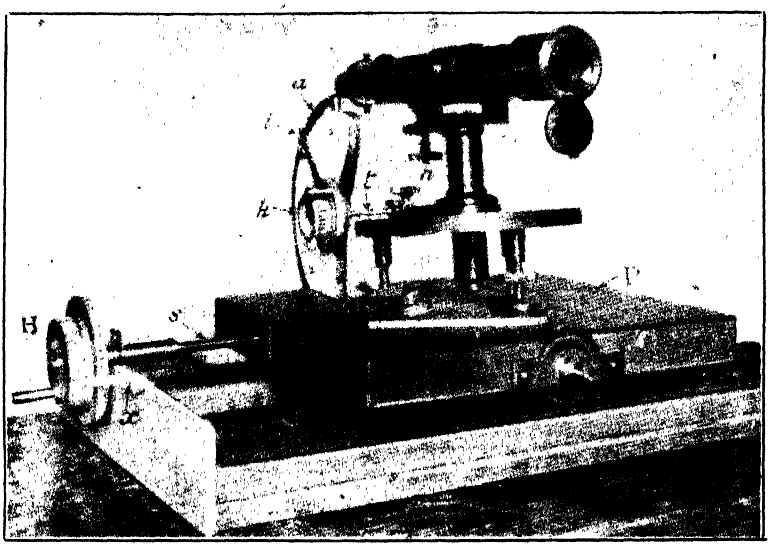


FIG. 19.

The distance between the balance and the telescope being 225 cm., it was found that when the coincidence of the cross-thread was transferred from one minor division of the beam to the next, the index *i* moved over an arc of 42 mm. Thus the precision with which the position of a rider was now determinable had been increased from an *estimated* $\frac{1}{10}$ to a *measured* $\frac{1}{42}$ of a minor division of the beam. Each arm of the beam had 50 divisions. Hence for the two riders, any one division corresponded to the respective values of $\frac{1}{5}$ and $\frac{1}{50}$ mg. ; and therefore by the device just described, the precision with which any positional value of the riders was now ascertainable was $\frac{1}{5} \times 42$ and $\frac{1}{50} \times 42$ mg. respectively.

The positions of the riders may also be measured with another equally precise micrometer, which, like that just described, is shown in Fig. 19. The instrument consists of an accurate screw *s*, having a pitch equal to a minor division of the beam, and a head H having 200 graduations. Rotational movements are measured with the aid of the plain index plate[1] *x* seen in the figure. For this micrometer the telescope is permanently set at right angles to the plane of the balance beam. In measuring a positional value, coincidence between the sighted rider and the vertical cross-thread is first established, this being accomplished by turning the head H. The micrometer is then read. Next H is again turned and the coincidence of the cross-thread transferred to one of the two adjacent beam divisions (say that nearest the central knife-edge), and the micrometer read a second time. Let the respective readings be r_1 and r_2 ; then in the case of the heavier rider, the small fractional weight under consideration is $r_1 - r_2/5 \times 200$ mg. Similarly for the other rider we have $r_3 - r_4/50 \times 200$ mg. Both values being positive are to be added.

It will be obvious that if for the second reading of the micrometer, the cross-thread coincides with the more distant of the two adjacent beam divisions, the weight so determined will have a negative value and is therefore to be subtracted.[2]

(15) *Invar Steel Balances.*—Messrs. L. Oertling have recently constructed high-grade precision balances having beams of invar steel formed as shown in Fig. 20. For ensuring accuracy, a plane mirror *m* is attached to the centre of the beam and use is made of a totally reflecting prism for directing the light incident from an electric lamp. The sensitivity S is given as 0·01 mg. ; but with a millimetre scale placed at a distance of 3 metres no difficulty is experienced in setting S as high as 0·002 mg. Through the courtesy of the makers we have been able to subject one of these balances to a series of tests.[3] Accordingly the beam was examined for (*a*) fatigue effects ; (*b*) variations in S with the load ; (*c*) possible effects producible by changes in temperature ; and (*d*) for fluctuations in the R.P. consequent upon changes in the enveloping magnetic field. We briefly consider each.

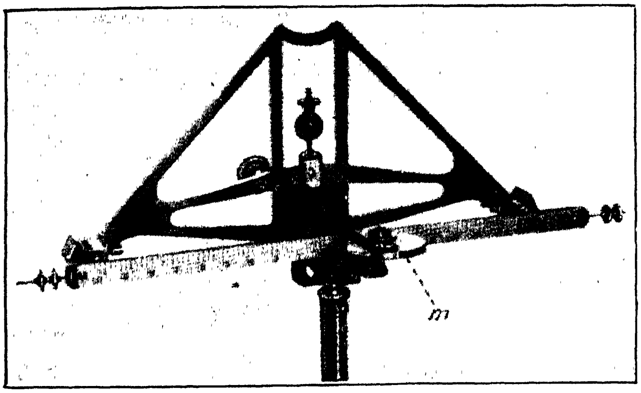


Fig. 20.

(*a*) In testing the beam for fatigue effects the imposed loads ranged from 0 (empty pans) to 200 g., the maximum load for which the instrument was built. The results showed that even if the maximum variation in the R.P. be wholly assigned to fatigue effects, the mean error would not have exceeded 0·02 mg. It was subsequently discovered that this variation of 0·02 mg. was in part due to convection currents operating upon the unshielded pans. Hence the errors due to fatigue were, in general, negligible ; and the conclusion reached was that the beam possessed rigidity of the highest order.

(*b*) In this the next series of experiments during which S approximated to 300 mm. per 1 mg., the sensitivity of the fully fatigued beam was determined as the load was gradually increased from zero to 200 g. It was thus found that for all loads exceeding 2 g. the mean variation in S was not more than $\pm\frac{4}{300} = \pm 0{\cdot}013$ mg. But as in the case of the experiments upon fatigue (*v. supra*), so here the variations in S were in all probability partially masked by errors introduced by the action of convection currents and therefore in the absence of decisive evidence, S could in general be regarded as a constant.

(*c*) In testing the balance for temperature effects, the plan adopted was that already described (*v. supra*). Now the coefficient of expansion for the beam under discussion was 87×10^{-8} ; also the length of the beam was 6 in. only. Under these circumstances it would therefore appear impossible that any *uniform* change in the temperature could produce *measurable* variations in the ratio of the lengths of the two arms. Therefore if it were possible to incorporate the three knife-edges in such a way that both they and the beam constituted a truly continuous whole, we should expect the temperature coefficient of the balance to be zero.

---

[1] For actual use this index plate is fixed behind H. Its temporary position in the illustration ensures clearness.

[2] *See also* Proc. Phys. Soc. 1927, **39**, 444–448.

[3] *Ibid.* 1926, **38**, 473–481.

But in this as in all other cases, we had before us a composite beam the component parts of which were held together and adjusted by means of screws; and these, in response to stresses accompanying changes in the temperature of the beam, might well become unequally strained; consequently the initial relative positions of the knife-edges might vary and thus alter the ratio of the length of the arms. The truth of this line of argument appears to be established by the results obtained with this particular beam and represented graphically in Fig. 21. The graph shows that the effect produced by increasing the temperature by 6°C. is equivalent to 0·008 mg. We also note that the values change first from positive to negative and then from negative to positive. Hence it appears that in the matter of relative movements and readjustments, predominance was acquired first by one group of screws and then by another. Had there been no relative movements of the knife-edges, the temperature coefficient of the beam would in all probability have been zero. We now briefly review certain observed magnetic effects and the consequences.

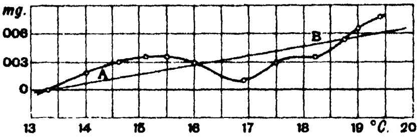


Fig. 21.

(*d*) For testing the behaviour of the balance in a variable magnetic field a 10-g. weight was first compared with a standard under normal conditions; and then in the presence of a thin bar magnet 1 m. long. The magnet was successively placed vertically over (1) the L-pan, (2) the central knife-edge, and (3) the R-pan. In each of these three experiments the distance between the lowest pole and the horizontal axis of the beam was 14 cm. The proximity of the magnet effected marked changes in the R.P.; but in each instance the new R.P. possessed a normal constancy. The results of the four standardisations are set forth below.

Conditions.	Normal.	Magnet over			Mean.	Difference between Mean and Normal Values.
		L-pan.	Centre of Beam.	R-pan.		
Weight	$9{\cdot}9988_8$	$9{\cdot}9988_8$	$9{\cdot}9988_4$	$9{\cdot}9988_7$	$9{\cdot}9988_6$	$-0{\cdot}00003=1$ in 333000

From the above we see that notwithstanding the magnetic character of the beam, the several values obtained for the weight are in remarkably good agreement; whence it appears that provided the method of Gauss be used, the results yielded by an invar steel beam can be but rarely influenced by changes in the intensity of the enveloping magnetic field; and even then such effects are in general almost, if not quite, negligible. Mention may now be made of yet another point.

When magnetic storms occur, the R.P. may be markedly affected. One such storm, which lasted for four days, was responsible for daily variations in the R.P. ranging from 32 to 67 scale divisions; and these were respectively equivalent to 0·105 to 0·220 mg.

Lastly, it may be remarked that in using a precision balance having an invar steel beam, due consideration should be given to the effects accompanying the normal daily variations within the local magnetic field. Occasionally these are appreciable and may not be neglected.

(16) *Aperiodic Balances.*—For some time past balances of the kind used by Madame Curie for her researches upon radium have come into use. In these balances a "dead-beat" action is obtained by the addition of concentric cylinders movable and fixed. The former are in some convenient way attached to the stirrups, whilst the latter are secured to the base of the instrument.

In some aperiodic balances the movable cylinders are suspended from an auxiliary pair of stirrups operating independently of those carrying the pans. By the introduction of this device, nothing beyond the usual care in loading is required. But in the absence of the auxiliary stirrups, it is imperative that the loads be carefully centralised; otherwise the damping cylinders are apt to make contact and thus nullify the accuracy of weighing. The reliability of the balance can at any time be quickly tested in the following way. The beam is released and the deflection noted; the rider is placed first at +1 mg. and subsequently at −1 mg., and corresponding readings taken. If the two deflections of the pointer are equal and opposite in sign, the condition of the damping apparatus is normal. Failing this, an inspection should be instituted and defects remedied.

When the pans are unequally loaded and released, suction operates within the one set of cylinders and a corresponding compression within the other. But when the loads are identical, equal and similar effects are manifested in both sets; and therefore in each case the vibrations of the beam are quickly suppressed.

The effectiveness of the damping largely depends upon the smallness of the interspaces of air; and this being so, close attention must be given to the state of the cylinders. Dust particles must be excluded; otherwise filaments become attached to the surfaces and bridge the intervening spaces, and thus produce a drag with its attendant uncertainties.

An aperiodic precision balance recently introduced by Messrs. L. Oertling is represented in Fig. 22.[1] Here the damping cylinders are placed in a line with the beam. Also, quite unlike precision balances in general, the beam is without a scale, and instead thereof use is made of an optical system O, G. Essentially, this consists of a finely divided scale or "graticule" attached to the end of the pointer, and a ground glass screen G upon which a central reference line L (Fig. 23) is drawn. When the graticule is electrically illuminated by a lamp placed behind the balance, an enlarged image of the same appears upon the screen. The graticule contains 500 divisions, and these represent 0·5 g. Each division is therefore equal to 1 mg. Tenths of 1 mg. are estimated. In Fig. 23 the fractional reading there shown is 0·3794 g. We observe that for a balance of this type all weights of less value than 0·5 g. are discarded, and in consequence the labour and tediousness usually attending accurate weighing disappear.

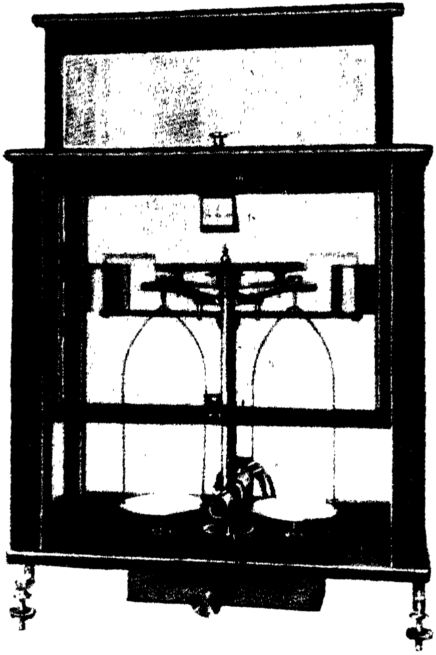


Fig. 22.

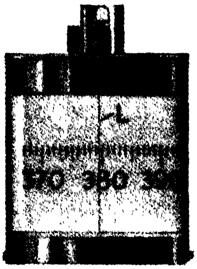


Fig. 23.

(17) *Micro-balances.*—For the accurate determination of extremely small masses, instruments known as *micro-balances* are used. These are of two types ; the action of the one depends upon torsion, and that of the other upon gravity ; but of the two the latter has been the more successfully and highly developed. Nernst and Reisenfeld (Ber. 1903, **36**, 2086) described a torsion balance sensitive to 0·0005 mg. with a load of several milligrams (for applications of same, *v.* Jänecke, Z. anal. Chem. 1904, **43**, 547 ; Brill, Ber. 1905, **38**, 140 ; Brill and Evans, Chem. Soc. Trans. 1908, **93**, 1442). The zero of this balance is inconstant, and its sensitivity varies greatly with the load. Gravity balances have been made by Steele and Grant (Proc. Roy. Soc. 1909, A. **82**, 580), and modified by Gray and Ramsay (*ibid.* 1911, A. **84**, 536 ; 1912, A. **86**, 270), to carry loads ranging from 1 or 2 mg. to 1 decigram with a sensitivity of 1×10^{-7} to 4×10^{-9} g. The zeros of these balances remain constant over long periods of time.

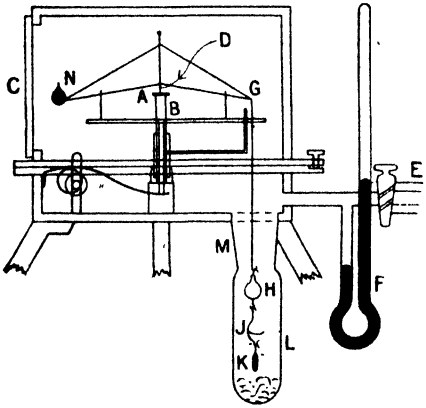


Fig. 24.

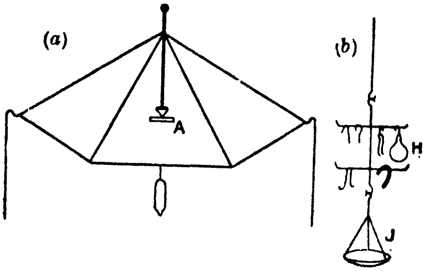


Fig. 25.

The beam, consisting of thin silica rods fused together to form a framework as shown in Fig. 24, has a length of 10 cm. (in Fig. 25 (*a*) a beam of a more rigid type is represented). The quartz knife-edge rests upon a highly polished and truly plane quartz surface secured to the top of the brass pillar B.

---

[1] For this illustration as well as for Figs. 24, 32, and 33 the writer is indebted to Messrs. L. Oertling, who very kindly granted the loan of the blocks and electros. Figs. 22 and 32 were specially prepared by them for this article.—J.J.M.

The vibrations of the balance are observed by means of a beam of light introduced through the window C and reflected by a tiny platinised quartz mirror fused to the beam at D ; with the mirror in this position, its angular movements are not accompanied by appreciable ones of a translational kind. The reflected light falls upon a vertical mm. scale placed at some convenient distance from the mirror. The three-way tap E allows the interior of the balance case to be put into communication with either the atmosphere or a vacuum pump ; the manometer F records the pressure within the case. A fine quartz thread fused to the beam at G supports (i) a sealed quartz bulb H of known volume V c.c. (either filled with air or vacuous), (ii) the scale-pan J, and (iii) a quartz counterpoise K. The whole hangs within the tube L (fitted to the case by the ground-glass joint M), and is counterpoised by a solid bead of silica fused to the beam at N. A little uranium oxide inside the case ionises the air and eliminates disturbing electrical effects ; and calcium chloride in L keeps the interior dry.

To perform a weighing, the pressure in the case is suitably lowered (to P_1 at temp. T_1 abs.), and the position of the reflected spot of light on the scale taken as the zero. The substance is then placed on the pan J, and a new pressure (P_2 at temp. T_2 abs.) determined under which the zero of the balance is recovered. The weight of the substance is then given by the expression

$$\frac{273V\sigma_0}{760}\left(\frac{P_2}{T_2}-\frac{P_1}{T_1}\right)$$

(σ_0=wt. of 1 c.c. air at N.T.P.)

The usual vacuum correction is, of course, necessary. Only weights less than the weight of air that the bulb H can hold may be thus determined. To measure greater weights, the counterpoise K is replaced by a lighter one ; a series of such counterpoises is required, and the differences between their weights may be measured on the micro-balance itself. It is convenient to make the bead N counterpoise the bulb, scale pan, and a set of weights (Fig. 25 (*b*)) (ranging from 2 to 0·1 mg. and made from capillary quartz tubing ; these are calibrated on the balance). In weighing a substance, weights are removed to obtain a coarse adjustment ; the pressure within the case is then altered, thereby making the (variable) buoyancy of the air on the bulb H effect the fine adjustment. The absolute accuracy of the weighings is limited to the accuracy with which V may be determined ; their relative accuracy is much greater.

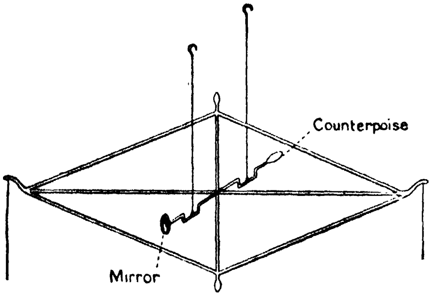


FIG. 26.

In a balance constructed by Steele and Grant, the beam, etc., weighed 0·93 g., the bulb H had a capacity of 0·422 c.c. and contained $5{\cdot}04\times10^{-4}$ g. of air ; the balance had a period of 33 secs., and was sensitive to 4×10^{-8} g.

The micro-balance of Gray and Ramsay has been modified by Hans Pettersson (Göteborgs, Vet. Vitterh. Samf. 1914, 14th series, xvi). In the altered form the central knife-edges are dispensed with, and the beam suspended, as shown in Fig. 26, by two thin quartz fibres, which are highly attenuated at their points of junction with the horizontal rod. Pettersson also greatly improved the balance case ; and for a vacuum-tight cement he uses an alloy having a low fusing-point. Further, the beam arrestment is magnetically controlled through the top of the balance case ; in this way errors due to possible air leakage are eliminated. R. Strömberg (Ann. Physik, 1915, **47,** 939) has improved the Pettersson balance and at the same time increased its sensibility by the substitution of detachable for fixed threads. The form of the Strömberg suspension is shown in Fig. 27, and the complete Pettersson-Strömberg beam and its accessories in Fig. 28. To the axial rod of the balance are attached (1) a tiny screw S for adjusting the centre of gravity, and (2) a minute plane mirror M for indicating with the aid of reflected light the angular position of the beam.

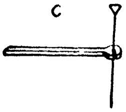


FIG. 27.

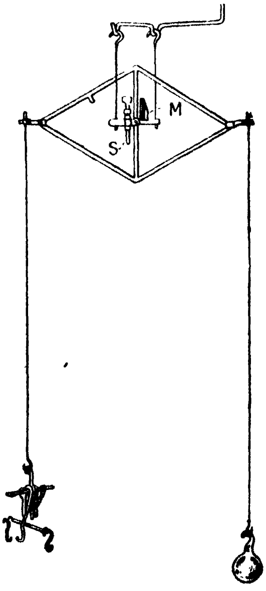


FIG. 28.

A section of the complete balance is shown in Fig. 29. An instrument of this type with its maximum load of 50 mg. may apparently have a sensitivity as high as ·01 μ-mg. The Pettersson-Strömberg balance has been used for testing the validity of Poynting's law at high temperatures, for measuring the volatility of silica at 800°C., and also for the accurate determination of the diamagnetic constants of gaseous hydrogen and nitrogen.

A simple form of micro-balance for determining the density of a gas has been described by F. W. Aston (Proc. Roy. Soc. 1914, A. 89, 439). The balance, which is made entirely of quartz, is represented in Fig. 30. The beam consists of two thin rods fused together as shown; the lower end of the shorter rod, *k*, terminates in a knife-edge which rests upon a quartz plane. To one end of the beam is fused a bulb *b*, having a capacity of about 0·3 c.c., and to the other the counterpoising rod *r*. The case, made of rectangular pieces of plate glass, is as diminutive as circumstances permit; the cell containing the beam is not more than 3 mm. wide, and its volume is a few c.c. only. A special chamber *c*, which is cemented to the left end of the case, is closed by the stopper *s*, which is pushed in until it just fails to touch the contained bulb. One limb of a T-tube having a capillary bore gives access to the interior of the balance case; the second limb is fused to a mercury manometer, and the third to a 3-way tap. By means of this tap communication between the balance and an air-pump or the gas-admission apparatus can be established. With the above-described apparatus the density of a gas is usually determined at a pressure of about 100 mm. of mercury. Measured at N.T.P., the volume of gas actually required for an experiment is approximately 0·5 c.c. A density determination is carried out as follows: The balance case is first highly exhausted, then the gas of which the density is sought is admitted until the bulb rises and the point *p* of the counterpoise appears in the field of a fixed reading microscope. The pressure is then varied until the beam comes to rest at some convenient but quite arbitrary zero, and the manometer read. Finally, the case is re-exhausted and the experiment repeated with a gas of known density. The ratio of the densities of the two gases is equal to the inverse ratio of the corresponding pressures. The determination can be made in a few minutes, and with an accuracy of from 0·1 to 0·01%. For accurate measurements Aston's micro-balance needs, no less than the heavier precision instrument (*v. supra*), a preliminary fatiguing. This operation appears to be best carried out by maintaining for some days a high vacuum within the balance case.

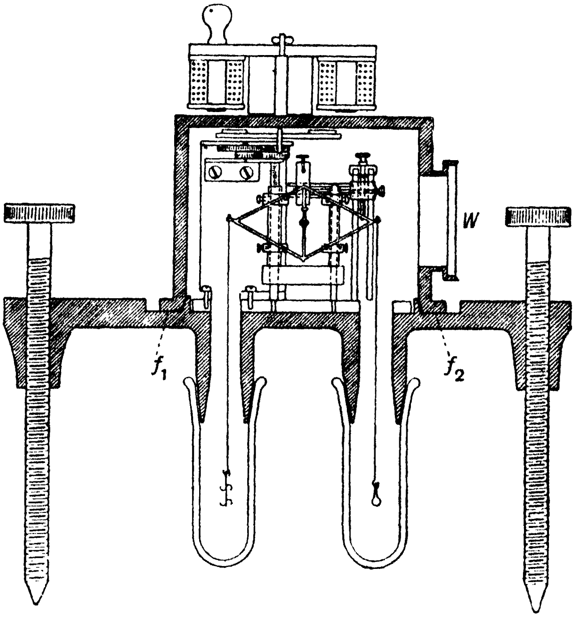


Fig. 29.

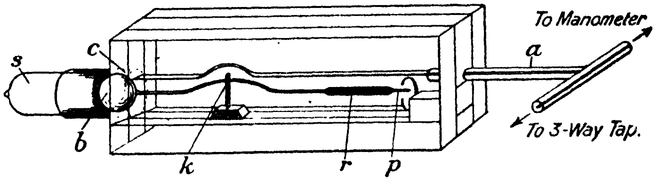


Fig. 30.

Riesenfeld and Möller (Z. Elektrochem. 1915, **21**, 131) describe a form of micro-balance for which they claim a sensitivity of $3{\cdot}3\times10^{-8}$ g., when the balance is carrying its maximum load of 5 mg. The beam is a glass capillary tube 13 cm. long; this is supported by a quartz thread attached at a point 3 cm. from one end. A mirror, made from a quarter of a microscope cover glass, is secured to the end of the shorter arm, and from the other end of the beam the pan is suspended. Various ways of supporting the pan are described, but the most successful for high sensitivity is that obtained by fastening a quartz thread horizontally and at right angles to the end of the arm. From this is hung the quartz thread which carries the pan. The arrestment consists of a clamp of two feathers, placed near the end of the longer arm.

Kramer (Chem.-Ztg. 1917, **41**, 773) has constructed a micro-balance of the usual type, with a carrying capacity of 1 g. The length of the beam is 154·4 mm., and the weight 7·825 g. When the balance is unloaded the sensitivity is equal to 48 divisions per 0·1 mg.; this decreases to 35 divisions for a load of 100 mg., and to 10 divisions for a load of 1000 mg. A division equals 0·35 mm.

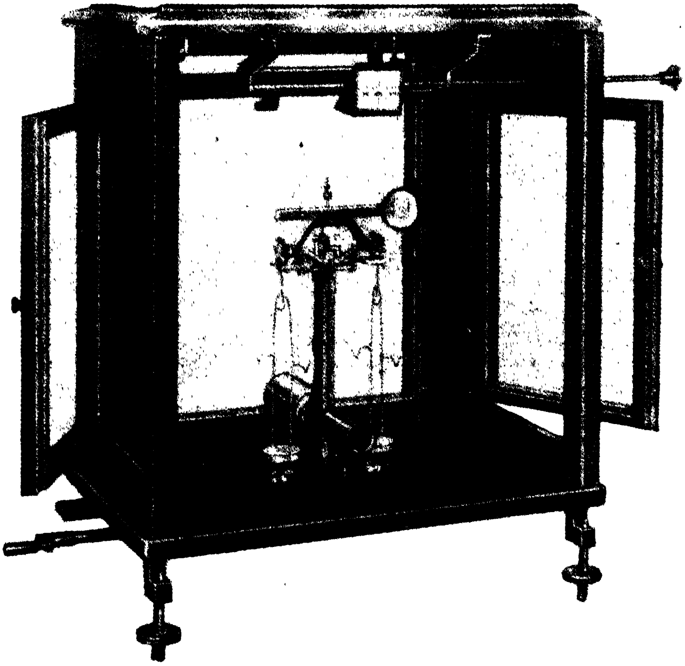


Fig. 31.—Prismatic Reflecting Micro-Balance.

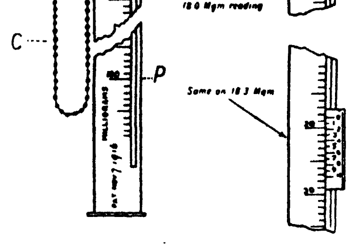


Fig. 32.

The *micro-assay balance*, known in Germany as a " Mikro-Chemische Wage," is a chemical balance in miniature; it stands as it were midway between the high-grade chemical balance of precision and the true micro-balance of Steele and Grant and others. The beam, which may have a carrying capacity of from 1 to 20 g., is rigid and exceptionally light; some of the more modern beams are also extremely short. First-class instruments have high sensitivities; hence, when lightly loaded the beam will usually indicate differences in weight ranging, according to the sensitivity of the balance, from ·05 to ·001 mg.

An excellent example of the micro-assay balance is depicted in Fig. 31. This instrument, lately built and introduced by Messrs. L. Oertling, has a beam the length of which is 3 in. only; its maximum load is 10 g. By means of a graticule and its associated optical devices clearly indicated in the figure and which are in all respects similar to those appertaining to the aperiodic balance depicted in Fig. 22 and already described in par. 16, a minimum mass of ·001 mg. is determinable. The smallest weight employed is 0·1 mg.: all lesser weights are directly shown by the graticule. Micro-assay balances differing in form but possessing similar sensitivities are obtainable from Kuhlmann of Hamburg and from other leading Continental makers. It may be unnecessary to remark that all those precautions already dealt with in connection with precision weighing in general are no less indispensable here.

(18) *Chainomatic Balances.*—We now pass to a brief consideration of the "chainomatic" balance, which has been largely developed and perfected in America. The earliest form of the instrument was, we believe, used, if not actually invented, by Sir Flinders Petrie. Such a balance has no rider, and all weights of less value than 0·1 g. are discarded. In place thereof use is made of a fine chain C (Fig. 32), one end of which is suspended from a point on the R-arm of the beam, whilst the other is carried by a hook secured to a vernier V. By means of a handle on the right-hand of the balance case the vernier can be made to traverse a linear scale inscribed upon a vertical pillar P ; thus the effective weight of the chain can be varied within the limits of 0 and 0·1 g., the smallest indicated weight being 0·1 mg. The device is applicable to precision balances in general. It is simple, highly convenient, and accurate.

ACCURATE DETERMINATIONS OF THE DIFFERENTIAL WEIGHTS OF GLASS VESSELS AND THEIR COUNTERPOISES.

(19) *Concerning the Wiping of Glass Vessels.*—For glass vessels which are to be weighed with any degree of refinement a most careful wiping is an indispensable preliminary ; and in making choice of material for the purpose, some discrimination must be shown. Theoretical considerations, verified by experiment, lead to the conclusion that in all probability it would be difficult to discover anything superior or equal to silk ; this substance possesses a very low heat conductivity ; and during use good specimens show a remarkably small tendency for casting off loose filaments. Objection is sometimes taken to the production of electric charges ; but from the practical point of view, the ground upon which the objection is based is more imaginary than real.

During the process of wiping, direct contact between the vessel and the hand must be scrupulously avoided ; more particularly so if we desire to maintain constancy of temperature. Some four or even more folds of silk should intervene between the hand and the vessel ; and if at the same time the hands are thickly gloved, so much the better. The vessel immediately after it has been wiped should be transferred to the pan of the balance with the aid of a suitable lifter. A slightly warmed vessel reassumes its original temperature with extreme slowness ; hence the desirability for guarding against any change in its temperature.

When the temperature of a sealed glass globe varies, two opposition factors operate and bring about an apparent change in weight. One is responsible for an apparent decrease in weight and the other for an apparent increase. An example will indicate the magnitude of each change. We consider the case of a globe having the volume of 100 c.c. and an apparent weight W in dry air when $t=15°$C. and $p=760$ mm. Let the coefficient of cubic expansion of glass be $=256\times10^{-7}$. Then for a variation of ±1°C., the change in volume is approximately ±·003 c.c. : hence the buoyancy varies by ±·001226× ·003 and the apparent weight by ∓·0037 mg. Next we observe that a change in the temperature of the globe is followed by some corresponding variation δt in the temperature and consequently in the density of the enveloping shell of air. Let the difference δt again be $=\pm1°$C. ; the change in the density of the air will then be ±·005 mg. and the apparent change in weight ±·005×100 mg. Hence for a variation in temperature $=\pm1°$C., the total change in the apparent weight of the globe is the sum of ±0·5 and ∓·0037 or ±0·4963 mg.

(20) *Of the Precautions to be taken in Weighing Glass Vessels.*—In weighing glass vessels, sealed or open, special difficulties other than those just considered are encountered. These chiefly arise from (1) the variableness of the water skin upon the surface ; (2) the fluctuating temperature and pressure of the air ; and (3) in the case of closed vessels, the inconstancy of volume resulting from changes in the temperature and effective pressure within ; the difficulties are still further accentuated when the vessel contains liquid matter, and more particularly so when the contents are solid. For many purposes the errors attendant upon causes (1) and (2) are sufficiently compensated by counterpoising the experimental vessels with others having very similar volumes ; but some cases demand additional precautionary measures. Such measures are called for when, from the nature of the investigation, equality of *area* as well as that of volume becomes a prime necessity. Now, although two volumes may, by trial, be adjusted to almost strict equality, to secure at the same time a similar equality of area is a highly difficult problem ; and yet, unless conditions are so ordered that a complete absence of moisture is ensured, a difference in the areas of a vessel and its counterpoise may well prove fatal to the object in view. This particular difficulty is surmounted in the following way :

A blower is formed by fitting up a large glass jar A, as shown in the self-explanatory Fig. 33. A slow working of the Bunsen water pump *p* is all that is required for keeping the jar full of air, the pressure of which is governed by the length of the tube supporting the bulb R. On leaving the jar by way of the tap *t*, the air is by means of two further taps (not shown) divided into equal streams ; each stream is driven first through a Drechsel wash-bottle, and then through a spiral glass tube, both charged with concentrated sulphuric acid. The stream on emerging from the spiral enters its own set of 3 purifying tubes ; the first half of each set is packed with small fragments of soda-lime, and the second half with similar pieces of calcium chloride. Finally, the air is filtered through glass wool or asbestos, and led, first through the walls of the balance case, and then through the upper ends of the cylinders surrounding the pans. From thence either stream is delivered through a glass jet directed downwards and placed centrally within its cylinder. With the above-described apparatus, any two objects (*e.g.* a closed vessel and its counterpoise), whose masses are to be subsequently compared, can be simultaneously subjected to a very perfect washing with air freed from carbon dioxide, moisture, and dust; this washing is allowed to proceed during the fatiguing of the beam. On escaping from the cylinders, the purified air displaces the ordinary air of the balance case; and as it is unnecessary to re-open the shutter before weighing, the operation is carried out within an atmosphere of standard and easily reproducible quality. A great convenience is secured if the air streams can be arrested by taps placed near the balance; these taps are closed just before the object is weighed. The plan here advocated has met with favour in several of the Oxford laboratories, where it has now been used for some years. The method might with advantage be universally substituted for the defective plan so commonly adopted with chemical and physical balances. To do this for any balance, it is but necessary to pass tubes delivering purified air through the top of the case just above the pans or in a line with the extremities of the beam. The usual method for drying the air within a balance case has several serious objections, which cannot be discussed here.

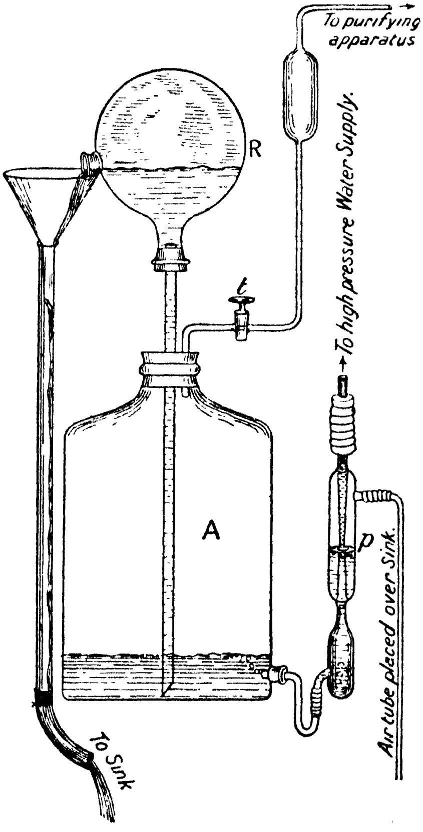


FIG. 33.

(21) *Of the Apparent Change in the Weight of a Cooling Body.*—When it is necessary to heat a body before its weight is determined, ample time must be allowed for the subsequent cooling. The time required for a hot body to assume the temperature of the balance case is greater than one would in general suppose. The importance of delaying the weighing until the object has acquired the temperature of the surrounding air is illustrated in Fig. 34.

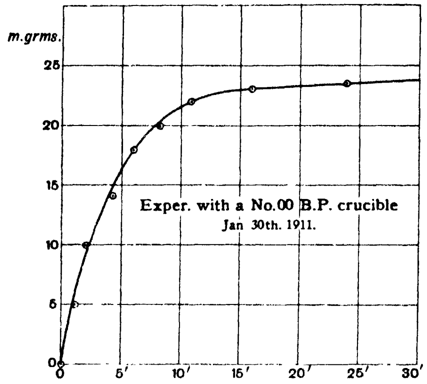


FIG. 34.

The data for the above graph was obtained as follows: A No. 00 B.P. crucible was heated to bright redness for some time and then removed from the flame. When the crucible was no longer *visibly* hot, it was placed upon the balance and immediately weighed under ordinary conditions; this weighing was followed by others at convenient intervals until 9 weighings in all had been carried out. During the period of half an hour required for the experiment, the weight of the crucible was constantly growing, at first rapidly, and then slowly; and notwithstanding the smallness of the mass, its limited surface, and the free cooling in air, the apparent weight of the crucible had not attained a maximum value when the experiment was terminated. The observed changes in the apparent weight result from a summation of various effects, of which the following appear to be the chief.

(i) An apparent *increase* in weight due to (*a*) the gradual re-condensation of moisture upon the glazed surface; (*b*) a slight increase in the length of the arm supporting the object pan; (*c*) the re-absorption of air and moisture by the porous mass of the crucible; and (*d*) the lessened buoyancy of the heated air immediately enveloping the crucible and balance pan.

(ii) An apparent *decrease* in weight due to ascending convection currents which tend to lift the object pan.

The lengthening of the balance arm noted in i (*b*) is effected by the heated air rising from the cooling crucible. The re-absorption of air and moisture (i (c)) by the general mass of the porcelain was rendered possible by the entire absence of glaze upon the bottom of the crucible. When the crucible is completely glazed, the internal condition of the porcelain remains presumably for all practical purposes strictly constant.

(22) *Of the Different Methods of Weighing.*—An article on weighing is incomplete unless it contains some allusion to the several methods available for accurate work ; but those methods are so well known both in theory and practice that the briefest outline will here suffice. To begin with, we take it as granted that an experimenter seeking for high precision would use the method of vibrations for ascertaining the R.P. of his balance. This matter has already been sufficiently dealt with by the late Prof. Dittmar. Secondly, apart from the common differential method used by chemists and physicists for much of their work, there remain (i) the method of Borda, and (ii) that introduced by Gauss.

(i) In Borda's method the object to be weighed is placed in either pan, and then accurately counterpoised by any convenient masses of unknown values ; such masses may consist of indifferent brass weights, lead shots, fine sand, etc. When the adjustment is complete, standard masses are substituted for the object, and these are varied until equilibrium has been re-established. Given unchanging conditions, it is obvious that the total weight of the standard masses equals the sought-for weight of the body. To this method may be opposed two objections : (*a*) its tediousness and (*b*) the impossibility of adjusting two initially different magnitudes to *precise* equality. These objections are so weighty that Borda's method is, comparatively speaking, but seldom used.

(ii) Following Gauss and using the method of vibrations, the R.P. is found with the object first in one pan and then in the other ; two determinations, d_1, d_2, of the R.P. are thus obtained. Then if S be the sensitivity of the balance in mg., the *difference* D between the weight of the standard mass employed and that of the object is given by the equation

$$D = \pm \frac{d_1 - d_2}{2} . S \text{ mg.}$$

and the apparent weight of the body is thus determined. The superiority of this method over others is based upon a principle well understood by physicists, viz. that in general it is easier to determine with accuracy by how much two magnitudes differ than to discover the true value of either.

For some further information upon the very important subject of highly refined weighing, the reader may be referred to (1) " The Limitations of the Balance," B. Blount, J.C.S. 1917, 1035 ; (2) " Vacuum Balance Cases," Blount and Woodcock, Chem. Soc. Trans. 1918, vol. cxiii, 81 ; (3) " Observations on the Anomalous Behaviour of Delicate Balances," Manley, Phil. Trans. Series A, vol. ccx, 387–415 ; (4) " On the Apparent Change in Weight during Chemical Reaction," Manley, Phil. Trans. Series A, vol. ccxii, 227–260 ; (5) " Observed Variations in the Temperature Coefficients of a Precision Balance," Manley, Proc. Roy. Soc. A, vol. lxxxvi, 591–600 ; and (6) " Dependence of Gravity on Temperature," Southerns, Proc. Roy. Soc. A, vol. lxxviii, 393 ; (7) " On the Use of Invar Steel for Precision Balances," Manley, Proc. Phys. Soc. 1926, **38**, 473–481 ; (8) " Observations Concerning Precision Weights," Manley, Phil. Mag. 1933, Ser. 7, vol. xvi, p. 489, Suppl. ; and (9) " Devices for ensuring Constancy in the Masses of Precision Weights," Manley, Phil. Mag. 1935, Ser. 7, vol. xix, p. 243. As the above third-named paper contains references to other papers bearing upon the same subject, it is unnecessary to repeat them here.

In conclusion, we may state that by availing ourselves of all precautions at present known to us, it has been found possible to attain an accuracy of ± 1 in 2×10^8 or thereabouts.

J. J. M.

THE CONRADY METHOD OF WEIGHING.

A method of weighing whereby an ordinary analytical balance can be adapted to give a very high degree of accuracy has been evolved by Conrady (Proc. Roy. Soc. 1922, A, **101**, (211)), as a result of an investigation of the sources of error involved in the normal use of the balance. A good balance should, of course, be so constructed as to be substantially free from the errors caused by mechanical defects such as loose agates, and by faulty design of the beam or suspensions, but apart from these there are sources of error which cannot be altogether eliminated by improvements in design and construction, and it was to minimise these errors that Conrady devised his method of weighing.

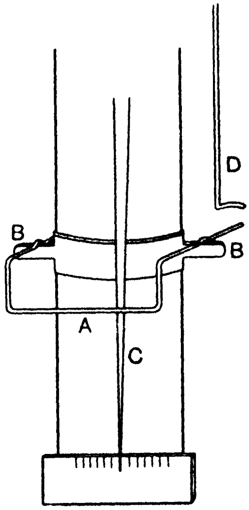


FIG. 35.—Form of Conrady Brake.

As the agate knife-edges are not perfectly sharp, but have edges with a definite radius of curvature, the motion when the balance is swinging is not a simple one about an axis, but rather a rolling on the arc which forms the edge of the knife. Therefore if in successive weighings the mean position of contact between the knife-edge and the plate varies, the length of arm error will not be constant and cannot be eliminated by double weighing, and this applies to all three knife-edges in the balance. A reasonably constant position of contact can be guaranteed only if the swinging of the balance is started without a jerk, a condition which can seldom be realised with the ordinary forms of release where one or more of the supports usually sticks slightly, giving a small uneven pull on the beam when it is released. To eliminate this jerk, Conrady fits a brake which is released and allows the balance to swing only when all the supports have been completely withdrawn, and there is therefore no danger of an uneven pull on the beam. A convenient form of brake is shown in the diagram. A piece of light but rigid wire A rests on the lugs BB and bears against the pointer C of the balance, these lugs BB being fixed to the balance pillar. Another piece of rigid wire D is fixed at its upper end to the beam support so that when this support has been lowered completely clear of the beam D then depresses the end of A, raising the front of it off the pointer and leaving the balance free to swing. This ensures that the knife-edges and agate plates make contact always in the same positions so that the length of arm error remains constant.

When a balance has been in use some time the lowest points of the knife-edges, the points which are first brought into contact with the plates, become worn and flattened, and it is then found that a definite overweight is necessary to start the balance swinging from the fictitious state of rest which the flat facets produce. To overcome this a permanent small overweight is added to one side of the beam so that the swings are all entirely to one side of the zero of the pointer scale, and the swinging then takes place on parts of the knife-edges which have not been flattened.

In addition to this permanent flattening due to wear, the agates are deformed by the pressure put on them each time the balance is in suspension, and as they are not perfectly elastic a certain amount of this deformation persists and gives a bias to the next weighing. This bias can, however, be eliminated by making the partial weighings in the following order, the swings, of course, always being on one and the same side of the zero. A preliminary weighing is first made with B, the mass to be weighed, in the left-hand pan and the counterpoising weights, A, in the right-hand pan. This gives an approximate weight and also adapts the knife-edges to the corresponding bias. The four partial weighings are then made.

(1) A in the left-hand pan and the deflection D_1 is determined from the pointer readings in the usual way.

(2) B in the left-hand pan, the deflection D_2 in this case being, of course, approximately that of the preliminary weighing.

(3) B still in the left-hand pan but with such a rider shift as will cause the deflection to be as nearly as possible equal to D_1. This rider shift can be readily calculated from the known sensitivity of the balance.

(4) A in the left-hand pan and with a rider shift to make the deflection nearly equal to D_2.

Weighing 1 gives A−B, affected with the bias produced by a change from the previous deflection D_2 (in the preliminary weighing) to the new deflection D_1.

Weighing 3 gives B−A with the same bias acting in the same direction as in weighing 1, although the masses have been reversed.

Hence the difference between weighings 1 and 3 gives twice the true difference between the masses A and B, *i.e.* 1−3=2(A−B).

In the same way this difference can be obtained from the weighings 2 and 4, and from the complete set of these weighings, known as the partial weighings, the effect of any progressive change in the balance can be cancelled out.

A very high degree of accuracy is claimed for this method of weighing. For example, an ordinary analytical balance fitted with the Conrady brake can be used for weighing fractions of a gram with an accuracy of 0·0005 mg., and a kilogram balance can in the same way be made to give an accuracy of 0·01 mg. J. L. B.

BALATA *v.* GUTTA.

BALLISTITE. This was one of the earliest military smokeless powders. It consists of approximately 50–60 parts of nitrocellulose and 50–40 nitroglycerin which are incorporated in the presence of hot water, agitation being effected by means of compressed air. The dough thus produced is then passed through heated rollers in order to expel excess water and convert the explosive into a sheet. The rolling process is repeated until the material is converted into a completely homogeneous colloid. The sheets, which may vary in thickness from about 0·007 to 0·028 in., are cut into square flakes which are usually coated with graphite and then blended. Various substances such as diphenylamine, aniline, and calcium carbonate have been added at different times in order to improve the stability of the powder.

Owing to the high temperature of explosion ballistite causes severe erosion of gunbarrels, and for this reason it has largely been replaced by powders containing less nitroglycerin.

Sporting ballistite is made in a similar manner to rifle ballistite except that acetone is used during the incorporation and the finished sheets are only about 0·005-in. thick. H. S.

BALM OF COPAIBA *v.* OLEO-RESINS.

BALM OF GILEAD. Mecca or Opobalsam (*v.* OLEO-RESINS).

BALSAMO BLANCO *v.* BALSAMS.

BALSAMS. There are a number of exudations from plants, some spontaneous, others induced by the making of incisions in the stems or roots; of the latter some are only formed by wounding the plant and may be regarded as pathological secretions. The word "balsam" is used *empirically*, and often overlaps the word "oleo-resin." Balsams are generally understood to mean exudations as above described, which consist of resins, sometimes with a little gum, some volatile oil, and usually with varying amounts of aromatic acids (such as cinnamic acid) and their esters. Where the essential oil is present in large quantity and the solid aromatic acids are absent, the substance is usually classed as an oleo-resin.

Most of the substances known in commerce as balsams are viscous or semi-solid bodies with a characteristic fragrant odour and of somewhat agreeable but pungent taste. The principal odoriferous ingredients are free benzoic, cinnamic, and closely allied acids and their esters, usually in the form of cinnamyl cinnamate, benzyl benzoate and cinnamate, and similar esters. Such bodies as Canada balsam and Copaiba balsam will be described under the title of OLEO-RESINS, as they consist entirely of solutions of solid resins in essential oils. The balsams to be described here are Benzoin, Peru, Storax, Tolu, and Xanthorrhœa.

Benzoin. (*Gum Benzoin : Gum Benjamin*).—The benzoin of commerce is either the product of *Styrax Benzoin* and allied species (N.O. Styraceæ), trees indigenous to Siam, Sumatra, and Java; or of *Styrax tonkinensis*, which furnishes the Siam benzoin of commerce (according to Drouet, "Les Parfums de France," 1924, **209**, the parent tree is *Anthostyrax tonkinensis*, Pierre). The principal commercial varieties are Sumatra and Siam benzoin, but the Palembang, Padang, and Penang varieties are also recognised, and are chiefly used in the manufacture of incense.

The trees do not normally produce benzoin, and the infliction of a wound sufficiently severe to injure the cambium is necessary to induce the formation of the balsam. It is therefore a pathological product. The trunk of the tree is usually hacked with an axe to make suitable incisions and the exudation collected. When it has hardened sufficiently it is exported either in the form of loose pieces (tears) or in masses.

Siam benzoin, which is highly valued, comes into the market both in tears and in masses, the latter consisting of tears cemented together with a transparent reddish-brown resin. It is characterised by its vanilla-like odour and its freedom from cinnamic acid. It is collected principally in the Siamese province of Luang Prabang.

Sumatra benzoin is obtained on the island of Sumatra, and is almost always exported in blocks, and not in tears. The better qualities have a fine storax-like odour, which is quite distinct from the vanilla odour of Siam benzoin. Sumatra benzoin is distinguished from Siam benzoin by the presence of cinnamic acid. If a little of the powdered balsam is boiled with a slightly acid solution of potassium permanganate, Sumatra benzoin will evolve the odour of benzaldehyde. Low-grade Sumatra benzoin, possibly obtained from different trees, or from exudations of trees which have become old and which only yield an almost inodorous exudation, is sold as *Penang benzoin*. *Palembang benzoin* also comes from Sumatra, but its origin is uncertain. Penang and Palembang benzoin are used in incense manufacture, and the Palembang variety also as a source of natural benzoic acid.

The commercial product contains varying amounts of extraneous impurities, and, assuming it is free from adulteration, benzoin may be judged by its solubility in alcohol, coupled with its odour value.

Unverdorben (Pogg. Ann. 1826, **8**, 397) and other early workers found that the resinous matter was not homogeneous, and distinguished fractions, according to their solubilities in various solvents, by the names α-resin, β-resin, etc. But this work is now only of historical value. Lüdy (Arch. Pharm. 1893, **231**, 43) showed that these substances were not individual compounds but were partially hydrolysed cinnamates of the resin alcohols present. He found in Sumatra benzoin, benzoic acid, styrene, traces of benzaldehyde and benzene (?), vanillin, phenyl-propyl cinnamate, cinnamyl cinnamate, benzoresinol cinnamate, and much suma-resinotannol cinnamate; the two last named bodies form the principal portion of the benzoin. Sumatra benzoin contains from 10 to 15% of benzoic acid and about 20% of cinnamic acid, mostly, of course, in the form of esters.

According to Lüdy (*ibid.* 461) Siam benzoin contains no cinnamic acid, the main constituent being a mixture of a little benzoresinol benzoate with much siaresinotannol benzoate. He was able to extract 38·2% of benzoic acid from the sample he examined. The alcohols, he stated, were present in the ratio of about 1 : 11. Benzoresinol crystallises in white prisms melting at 272°. Siaresinotannol, $C_{12}H_{14}O_3$, is a brown powder.

The most recent examination of Siam benzoin, however, is that by Reinitzer (Arch. Pharm. 1921, **259.1**, 60). He states that he has isolated a small quantity of siaresinolic acid, $C_{30}H_{48}O_4$, m.p. 260°, and that the benzoic ester of an alcohol, which is termed *lubanol*, is a characteristic constituent of Siam benzoin; it has the formula $C_{17}H_{16}O_4$, and forms crystalline plates, m.p. 72·8°. Benzoin is official in the British Pharmacopœia (1933), which authority prescribes the following requirements for the balsam which is to be used for medicinal purposes.

It must contain not less than 19% and not more than 29% of free balsamic acids, and not less than 30% and not more than 60% of total balsamic acids, both calculated on the dry alcohol-soluble matter. The residue after extraction with 90% alcohol, and being dried at 100° shall not exceed 20%. The loss on drying in vacuo over sulphuric acid shall not exceed 10%. The alcohol-soluble matter shall have an acid value 115–163 ; ester value 47–83 ; and saponification value 169–223. The ash content of the sample shall not exceed 2%.

Benzoin is used in medicine and in perfumery and forms a constituent of most types of incense.

Cocking and Kettle have published the following figures for a number of samples of benzoin (Trans. Brit. Pharm. Conference, 1914, 357). The analytical values are for the alcohol-soluble matter. (See table on page 616.)

Solubility in Alcohol 90%.	Acid Value.	Ester Value.	Free		Total Aromatic Acids.
			Benzoic Acid.	Cinnamic Acid.	
%			%	%	%
66·3	140·3	64·1	6·92	9·08	26·69
65·4	139·9	83·2	6·11	10·73	28·48
94·1	127·0	63·2	1·12	17·0	35·94
67·0	132·8	65·2	7·52	8·68	25·06
71·9	137·1	68·4	6·26	9·76	27·40
98·8	142·4	65·2	22·34	1·16	39·23
94·7	137·5	65·8	21·47	2·68	39·45
73·3	142·1	56·5	8·21	13·21	28·50
83·1	122·9	56·0	19·33		25·30
72·7	122·0	47·0	18·31		22·71
71·6	122·3	81·5	14·0		21·56

To determine the total balsamic acids, Cocking and Kettle extract 5 g. with alcohol and hydrolyse the extract with alcoholic potash. The alcohol is evaporated, the residue dissolved in 100 c.c. of water, acidified with HCl, and then 5 g. of magnesia and 20 c.c. of xylene are added. The mixture is boiled for an hour under a reflux condenser, the aqueous liquid separated, and the insoluble matter extracted twice with boiling water, which is cooled before filtration, and the combined aqueous liquids, after extraction once with ether, are acidified, and the liberated balsamic acids extracted with ether in the usual way.

Cocking (Quart. J. Pharm. 1931, **4**, 330) has improved the above method for the determination of the aromatic acids in balsams as follows. The balsam is saponified with seminormal potash, the liquid evaporated to dryness, dissolved in water, and the Mg salts of the resin acids precipitated by a solution of $MgSO_4$. The filtrate is acidified and extracted with ether, and the ethereal solution, containing aromatic alcohols, as well as free acids, is extracted with a 5% solution of $NaHCO_3$ to extract the balsamic acids.

Peru (Balsam of).—Balsam of Peru is a dark brown viscid liquid, somewhat resembling molasses in appearance. It has a powerful, pleasant and balsamic odour, recalling that of vanilla. It is used to a considerable extent in perfumery, forming a useful ingredient in heavy odours of the "amber" or Oriental types. It is obtained from the trunk of the tree *Myroxylon Pereiræ*, a tree flourishing in the forests of San Salvador, in Central America. The balsam is not a normal secretion, and may be described as a pathological product, the formation and flow from the tree being induced by gently heating the bark, and subsequently scorching the trunk. As the balsam flows from the tree it is absorbed by cloth which is used to cover the wounds of the tree. The cloths are pressed, and the balsam so obtained is purified by boiling with water.

Balsam of Peru has a specific gravity of 1·140 to 1·170 and refractive index 1·580 to 1·586. It is official in the British Pharmacopœia (1932), which authority requires it to contain not less than 53% of balsamic esters, the saponification value of which shall not be less than 235. The earliest analysis of any value is that of Kachler (Ber. 1869, **2**, 512). He stated that it contained 46% of cinnamic acid, 20% of benzyl alcohol and 32% of resin. Generally speaking, Balsam of Peru contains from 50 to 65% of a colourless, oily liquid, and about 30% of dark coloured resin. The aromatic oily liquid is usually known as *cinnamein* and consists of a mixture of benzyl benzoate and benzyl cinnamate in varying proportions, together with esters of an alcohol, *peruviol.* Peruviol (Thoms, Arch. Pharm. 1899, **237**, 271) has a honey-like odour, and is probably identical with nerolidol, $C_{15}H_{26}O$, each yielding a phenyl-urethane, m.p. 37°–38° (Schimmel, Report, April, 1914, 80).

Traces of farnesol vanillin and free cinnamic acid are also present. The resin consists of the cinnamic and benzoic esters of an alcohol to which the name *peruresinotannol* has been given. The empirical formula $C_{18}H_{20}O_5$, has been assigned to this alcohol. The old-fashioned adulterants of Balsam of Peru, such as turpentine, gurjun balsam and the like are not used to-day. Fixed oils lower the specific gravity so much that they are readily detected, and the fatty acids which they yield on saponification are easily identified. A more common adulterant is the artificially prepared benzyl benzoate, which usually increases the content of so-called cinnamein, and may be detected by a systematic examination of the products of saponification, when an undue preponderance of benzoic acid over cinnamic acid will be found. According to Janot (Bull. Sci. Pharm. 1934, **41**, 219) the cinnamein value for pure Balsam of Peru is 52–54%; saponification value 243–246 and iodine value 35·8–36·7. Dieterich has given the following values for three samples of authentic origin :

	1.	2.	3.
Acid value	77·46%	76·92%	77·34%
Ester value	165·6	137·4	137·7
Cinnamein	71·4%	77·6%	73·6%
Resin esters	15·7%	13·2%	17·3%
Insoluble in ether	4·38%	4·31%	3·57%

The so-called "White" Balsam of Peru—or Balsamo blanco—is possibly identical with American storax, derived from *Liquidambar styraciflua* (*v.* STORAX).

Peru balsam is used to a small extent in medicine and to a considerable extent in perfumery. It has a heavy odour and has great fixative value. It is also used to a considerable extent in the preparation of so-called "artificial amber."

A balsam closely resembling Peru balsam has been described by F. W. Freise (Pharm. Zentr. 1933, **74**, 223). It is obtained in Brazil from *Myrocarpus fastigatus*, and has *d* 1·1315 to 1·1665, n^{25} 1·5662 to 1·6318, and saponification 212 to 255. Its cinnamein content varies from 48·5 to 67·5%.

Storax.—Storax or styrax is the purified balsam, obtained from the trunk of *Liquidambar orientalis*, a tree belonging to the Hamamelidaceæ, and which is indigenous to the south-west of Asiatic Turkey. The balsam is not a normal secretion of the tree, being induced by wounding the bark. The tree is usually beaten in the summer time, and the cambium is injured, and oleo-resin ducts are formed in which the balsam is secreted and is discharged therefrom into the wounded bark. Secretion can also be induced by making incisions in the bark. The bark is removed, and the balsam separated by pressing and boiling with water. The water is removed, and the crude storax thus obtained is an opaque, greyish, viscid liquid, containing fragments of bark and other debris, and from 20 to 30% of water; it is purified by solution in 90% alcohol, filtration, and evaporation.

The product is the prepared storax of medicine. The British Pharmacopœia (1932) gives the following standards for the medicinal balsam:—"The sample, dried on the water bath for one hour, should contain not less than 30% of balsamic acids. The loss on drying on a water bath should not exceed 5%. The dried sample should have an acid value 55 to 90; ester value 100 to 133; and saponification value 170 to 200."

Storax—that is the purified balsam separated from water and alcohol-insoluble matter—is a highly viscous liquid of pleasant balsamic odour, and is used both as a fixative in perfumery, and in heavy perfumes of the oriental type as an odorous constituent. It consists of a resinous material mixed with an oily liquid. The resin contains an alcohol or mixture of alcohols, known as *storesinol*, partly free and partly combined with cinnamic acid. The liquid portion contains phenylethylene $C_6H_5{\cdot}CH{:}CH_2$ (styrene or styrolene), vanillin, and free cinnamic acid, and the esters of this acid with ethyl, benzyl phenyl-propyl, and cinnamyl alcohols. Traces of free cinnamic alcohol are present, and a minute quantity of naphthalene. Cinnamyl cinnamate is also known as *styracin*. The older examinations of storax are now only of historical interest. A good bibliography of the subject will be found in von Miller's memoir on the Chemical Compounds contained in Liquid Storax (Annalen, 1877, **188**, 184).

Purified storax should have the following characters:

Specific gravity at 100° .	1·105 to 1·115
Acid value.	55 to 95
Ester value	90 to 150
Total cinnamic acid . .	25 to 35%

Rarely a higher amount of cinnamic acid may be present. There is a good deal of so-called storax, from which much cinnamic acid has been removed and replaced by colophony. Any sample containing under 25% of cinnamic acid should be very carefully examined, the Storch reaction being applied. The prepared storax of medicine must not be confused with the "storax" of the ancients, which was investigated by Hanbury in 1857; he concluded that the storax described by Dioscorides, Pliny and others was the solid resin, obtained in agglutinated tears, resembling benzoin, obtained from the trunk of the tree *Styrax officinale*. This "storax" is not now an article of commerce.

The so-called *American storax* is the product of *Liquidambar styraciflua*, and yields about 85% of purified balsam, which has the following characters:

Acid value	up to 40
Ester value	up to 140
Specific gravity . . .	1·140 to 1·160
Refractive index at 25° .	1·588 to 1·595

It yields an essential oil of specific gravity 0·950 to 1·050; refractive index 1·5395 to 1·5653, containing phenylethylene, esters of cinnamic acid, vanillin and free alcohols.

Tolu.—Balsam of Tolu appears to have been first referred to by Monardes in his work on the products of the West Indies published in 1574. It is obtained from the trunk of *Myroxylon toluifera*, one of the *Leguminosæ*, a tree indigenous to New Granada, and found in Venezuela, Ecuador and Brazil. Considerable quantities are exported from Bolivia. V-shaped incisions are made in the trunk and the exudation, which flows for about eight months of the year, is collected in gourds and ultimately exported in tins. It is a soft, tenacious, resinous substance, which hardens on keeping and is brittle in the winter. It has a fragrant odour and an acid taste and is used in the preparation of perfumes of the heavy oriental type and as a perfume fixative. If a small piece be warmed and pressed between two pieces of glass, crystals of cinnamic acid can be seen with the aid of a lens. Balsam of Tolu contains from 12 to 15% of free cinnamic acid and from 7 to 10% of free benzoic acid. Up to 8% of an oil consisting mainly of benzyl esters of cinnamic and benzoic acids is present, and traces of vanillin have been identified. The resinous matter consists mainly of the cinnamic and benzoic esters of a complex alcohol to which the name *toluresinotannol* has been given, and the formula $C_{17}H_{18}O_5$ assigned.

Balsam of Tolu is soluble in alcohol, benzene, chloroform, ether and glacial acetic acid. It is official in the British Pharmacopœia, and the official requirements of the 1933 edition are as follows. It contains not less than 19% and not more than 25% of free balsamic acids, and not less than 35% or more than 50% of total balsamic acids, each calculated on the dry alcohol-soluble matter. The loss on drying in a thin layer in vacuo over sulphuric acid should not exceed 4%. Matter insoluble in alcohol should not exceed 4%. The alcohol-soluble matter should have an acid value 97 to 160; ester value 47 to 95; and saponification value 170 to 224. The balsam must not show any reaction for colophony. Cocking and Kettle ("Year Book of Pharmacy," 1918, 407) give the following values for 14 genuine samples of Balsam of Tolu, and also give a detailed method of analysis:

	Acid Value.	Ester Value.	Free Benzoic Acid.	Total Balsamic Acids.
			%	%
1	111·8	71·2	8·55	32·66
2	112·3	79·0	9·12	35·08
3	98·1	79·1	8·48	37·37
4	100·6	72·2	7·80	34·86
5	118·2	60·8	9·10	37·71
6	92·2	62·6	6·63	33·87
7	101·3	65·9	8·29	37·50
8	102·5	59·3	8·34	36·18
9	96·6	65·0	7·86	37·36
10	132·4	66·2	7·42	39·86
11	140·1	39·4	—	24·74
12	124·3	58·3	—	24·40
13	117·8	90·9	—	47·56
14	108·9	85·3	—	45·12

C. T. Bennett (Perf. and Essent. Oil Rec. 1928, **19**, 464) considers that the acid values from 112 to 168, and saponification values 154 to 220 cover all genuine samples.

Xanthorrhœa balsams.—There are several balsamic exudations from species of *Xanthorrhœa*, especially *X. australis*, plants found over a wide area of the Australian continent. The balsams are usually referred to as *acaroid resins*. Two principal varieties are known, the red and the yellow resins. The red variety is also known as "grass tree gum" or "Blackboy gum"; whereas the yellow variety is often termed "Botany Bay gum," and is exported chiefly from Tasmania. There is a pale variety obtained in New South Wales, which, according to Umney (Perf. and Essent. Oil Rec. 1915, 212) is derived from *X. hastilis*, and a dark variety obtained from *X. arborea*. The former is very aromatic and contains benzoic acid. It can be used in perfumery as a substitute for benzoin, storax and tolu, and it may be used as an incense resin as it burns with a fragrant odour. It also finds employment in the manufacture of cheap sealing wax and japanner's gold size and in stains for wood. For a description of the various types of balsams yielded by a number of species a paper by Andés (Chem. Rev. Fett. Harz. Ind. 1909, **16**, 160) should be consulted. According to Hildebrand (Arch. Pharm. 1896, **234**, 698) the compositions of the yellow and red resins are very similar, the principal difference being that the former contains cinnamic acid. In the red resin (*X. australis*) he found a small quantity of *p*-coumaric acid, and the ester of this acid with the alcohol erythro-resinotannol $C_{40}H_{39}O_9{\cdot}OH$, which forms the chief part of the resin. Traces of benzoic acid and *p*-hydroxybenzaldehyde were also found. The yellow resin contains free coumaric acid, a little free cinnamic acid, and each acid is present as the ester of the alcohol *xanthoresinotannol* $C_{43}H_{45}O_9{\cdot}OH$, which constitutes the chief part of the resin.

The red acaroid resin from the West Indies is very similar to the Australian resin, but it contains cinnamic acid, which is not present in the red Australian variety. Xanthorrhœa resin was suggested by Stenhouse (Annalen, 1846, **57**, 84) as a source of picric acid, which it yields on treatment with nitric acid, and a certain amount of the explosive was thus made during the Great War.

According to Rudling (Chem. Rev. Fett. v. Harz. Ind. 1903, **10**, 51) the yellow resin has an acid value 64 to 88, saponification value 98 to 176·4, and iodine value 175–191·5. Rebs (Lack u. Farben. Ind. 1908, 11) gives the following method for identifying acaroid resin in the presence of manila, shellac, sandarac and colophony. A small amount of the material is heated with 10 to 20 drops of nitric acid until nitrous fumes are copiously evolved. When cold the residue is dissolved in alcohol, and 10 drops of a 5% solution of ferric chloride are added. A brown or blackish-brown colour, together with turbidity of the liquid, denotes the presence of acaroid.

Schimmel & Co. (Report, Oct. 1897, 60) give the characters of the essential oil from the yellow resin as follows: specific gravity 0·937, optical rotation −3° 14′, acid value 4·9, and ester value 69·4. The oil from *X. australis* has specific gravity 0·963, optical rotation ±0°, acid value 47·6, and ester value 37·5 (Haensel, Apoth.-Ztg. 1908, **23**, 279). Rennie, Cooke, and Finlayson (J.C.S. 1920, **117**, 338) have investigated a *Xanthorrhœa* oil of unknown botanical origin, which was found to contain *pæonol* as almost its only constituent. This body, $C_9H_{10}O_3$, is *p*-methoxy-*o*-hydroxy-phenyl methyl ketone. The essential oil of *X. Tateana* contains pæonol and hydroxypæonol, and that from *X. Preissii* contains pæonol, hydroxypæonol, and probably methoxy-diphenyl ether.

For the latest contribution to the description, botanical derivation, and commerce of the acaroid resins, Bulletin No. 16, Technological Museum, Sydney, N.S.W. 1931 (by A. W. Penfold) should be consulted. E. J. P.

BAMBARA-FAT or **BAMBOOI-FAT** *v.* Bassia Fats.

BAMBOO. The ash of the shoots of these grasses (*Bambusa arundinacea* (Willd), *Gigantochloa verticillata* (Munro), etc.) contains from 30 to 40% of K_2O, and constitutes a potential source of potash. The fibres of the shoots supply an excellent paper-making material, and have been used for this purpose by the Chinese from time immemorial (Romanis, Chem. News, 1882, **45**, 158; **46**, 51; Nature, **18**, 50).

BAMBOOI-FAT or **BAMBARA-FAT** or **BAMBUK BUTTER** *v.* Bassia Fats.

BAMBUK BUTTER *v.* Bassia Fats (Shea Butter).

BANANA. The fruit of various species of the genus *Musa*, typically *M. sapientum*, L., but now much more commonly, the plantain or plantain banana (*M. paradisiaca*, L.). All are of tropical origin but are readily transported if picked green. The green fruit has a high starch content and very little sugar. In this stage the flesh may be dried, ground and marketed as banana meal or flour, an easily-digested foodstuff. "Pisang" (banana) flour from the Dutch Indies has the following percentage composition:

Water.	Protein.	Fat.	Starch.	Ash.
12–13	3–4	0·5–1·0	72–73	2·0–2·2

The ripening process is characterised by a rapid conversion of starch to sugars and may be hastened by exposure to ethylene (Wolfe, Bot. Gaz. 1931, **92**, 337). Recorded analytical data show varietal differences in carbohydrate composition, but the following ranges of values serve as a general comparison of green and ripe fruit (as percentage of dry matter):

	Starch.	Sucrose.	Reducing Sugars.
Green .	64–74	0·0–0·4	0·0–1·8
Ripe .	5·2–14·5	6·6–30·1	20–40

The wide variations in analyses of ripe fruit are to be anticipated from the very divergent views as to what constitutes actual ripeness, and are accentuated by the fact that in the earlier stages of ripening the sucrose content tends to increase more rapidly than that of reducing sugars, whereas in the later stages the order is reversed, *see* Bailey (J. Biol. Chem. 1906, **1**, 355); Gore (J. Agric. Res. 1915, **3**, 187); Kondo *et al.* (Mem. Coll. Agric. Kyoto, 1928, **6**, 23).

The ripe fruit contain appreciable amounts of amyl acetate, which is partly responsible for the characteristic odour, *see* Kleber (Amer. Perfumer, 1913, **7**, 235).

According to Von Loesecke (J. Amer. Chem. Soc. 1929, **51**, 2439) the green fruit has from 50 to 1,000 mg. of chlorophyll (α and β) per kg. of fresh peel. The yellow pigments of ripe fruit consist mainly of xanthophyll (5·2–7·3 mg.) and carotene (1·2–3·7 mg.) per kg.

Other recorded constituents include organic acids (principally malic), 0·9–1·4%, tannin 0·3–1·7%, and pectin 1·0–1·5%.

As typical general analyses the following may be cited:

Origin.	Water.	Protein.	Fat.	Total Sugar.	Starch.	Fibre.	Ash.
Cuba .	72·5	1·16	—	20·2	—	—	0·86
Surinam	74·8	1·72	—	19·4	1·3	0·62	0·9
Hawaii.	71·8	1·4	0·2	20·2	—	0·37	0·72
?	73·8	1·33	0·25	19·6	—	0·8	0·9

König (Chem. mensch. Nähr.-Genussm. 1920, **2**, 877) gives the following ash analysis, the ash constituting 0·7–1·2% of the fresh fruit.

K_2O	52·64
Na_2O	2·76
CaO	1·17
Fe_2O_3	0·39
Mn_3O_4	0·58
MgO	5·36
P_2O_5	6·12
SO_3	3·45
SiO_2	2·33
Cl	11·64

The high figure for potassium common to peel and pulp has suggested the collection of banana waste, the ash of which would form a valuable fertiliser. Among the "trace" elements examined by various authors may be mentioned **Cu**, **Al**, and **Zn** present to the extent of several mg. per kg. of fruit, and **As** (0·06 mg. per kg.). A. G. Po.

BANISTERINE-HARMINE *v.* HARMALA ALKALOIDS.

BAOBAB TREE *v.* ADASONIA DIGITATA.

BAPHIC ACID *v.* BARWOOD.

BAPHIIN *v.* BARWOOD.

BAPHNITIN *v.* BARWOOD.

BAPHNITONE *v.* BARWOOD.

ψ-BAPTIGENIN *v.* BAPTISIN.

BAPTIN *v.* BAPTISIN.

BAPTISIA TINCTORIA (Fam. Leguminosæ). Wild Indigo Root. Contains a blue dye which has been used as an inferior substitute for indigo, the poisonous alkaloid *cytisin*, also found in laburnum and gorse, and a glucoside ψ-baptisin, together with a crystalline substance with purgative properties.

BAPTISIN, $C_{26}H_{32}O_{14}$, m.p. 244°, $[\alpha]_D^{20}$ $-61·7°$, the glycoside of the roots of *Baptisia tinctoria*, is hydrolysed by sulphuric acid to glucose, rhamnose and ψ-baptigenin, which is 7 - hydroxy - 3′ : 4′ - methylenedioxy*iso*flavone (Finnemore, Pharm. J. 1910, 604). The roots contain a small quantity of a further glycoside, *baptin*, m.p. 188°. E. F. A.

BARATOL. An explosive containing barium nitrate and trinitrotoluene, the proportions of which may be varied to suit the required purpose. A mixture containing 80% T.N.T. and 20% barium nitrate has been largely used. Baratol possesses advantages over amatol in being non-hygroscopic and practically non-corrosive. On the other hand, the barium radicle, with its relatively high atomic weight, is practically inert from the explosive point of view, and the resulting high density of loading is not accompanied by a corresponding increase in explosive power. H. S.

BARBATIC ACID *v.* LICHENS.

BARBATOLIC ACID *v.* LICHENS.

BARBERRY. Barberry or berberry, *Berberis vulgaris*, is a compact bush which attains a height of from 8 to 10 ft., and is found wild in Great Britain and throughout most parts of Europe and North America. The colouring matter present is *berberine*, and this, though occurring mainly in the bark, is also present in the stem and root of the plant.

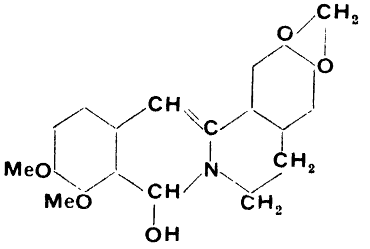
A concentrated commercial extract of this material, known as "Barberry extract," was at one time to be found on the market and was employed for dyeing silk and leather, although it does not appear to have been at any time extensively used for this purpose.

Barberry is, however, interesting, in that it contains the only natural basic dyestuff at present known, and may, in fact, be applied to fabrics in the same way as the artificial basic colouring matters. Silk and wool, for instance, may be dyed yellow by means of a faintly acidulated decoction of the material, preferably at from 50° to 60°, whereas for cotton, a tannin-antimony mordant is necessary.

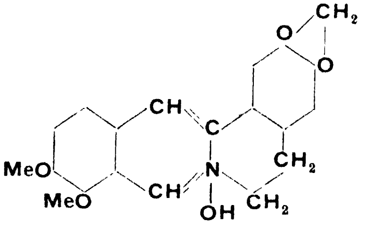
For the isolation of berberine the procedure is simple, and consists merely in extracting the ground dyestuff with boiling water containing a slight excess of lead acetate. The concentrated extract, when mixed with hydrochloric acid and cooled, deposits yellow needles of berberinium chloride, $C_{20}H_{18}O_4NCl$. The base berberine,

$C_{20}H_{19}O_5N$, is best obtained by adding strong caustic soda to the aqueous solution of the sulphate and extracting with ether, from which it separates in yellow needles, m.p. 144°.

Our knowledge of the structure of berberine is mainly due to the work of W. H. Perkin (J.C.S. 1899, **55**, 75, *et seq.*), who concluded that berberine is represented by formula (I), and that for the purpose of salt formation it undergoes change into the modification called berberinium hydroxide (II), in which the hydroxyl group is replaced by the acid radical.



I.



II.

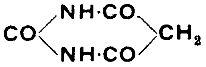
Numerous plants contain berberine, and though most of these have been or are used medicinally, their employment for dyeing has apparently been of rare occurrence. The following list embodies most of these:

Berberis aquifolium (Gordin, Arch. Pharm. 1902, **240**, 146), *B. heteropoda* (Orekhov, *ibid.* 1933, **271**, 323), *B. laurina*, Billb. (Thunb.) (de A. Costa and da Silva, Rev. Soc. Brasil. Quim. 1933, **4**, 199; Boll. Assoc. Brasil. pharm. 1934, **15**, 11), *B. oetnensis* (Perkin, J.C.S. 1897, **71**, 1198), *Coeloeline polycarpa* (Stenhouse, Annalen, 1855, **95**, 108; 1858, **105**, 360), *Coptis aceta* and *C. trifolia*, *Chelidonium majus* and *Stylophorum diphyllum* (Schlotterbeck, Amer. J. Pharm. 1902, **74**, 584), *Coptis occidentalis* (Mollett and Christensen, J. Amer. Pharm. Assoc. 1934, **23**, 310), *Cossinium fenestratum* and *Xanthorrisa aquifolia* (Perrins, Annalen, 1852, **83**, 276), *Evodia melisæfolia* and *Toddalia aculeata* (Perkin and Hummel, J.C.S. 1895, **67**, 414), *Hydrastis canadensis* (Mahla, Sill. Am. J. 1862, (2) **33**, 43), *Mahonia nepalensis* (D. C.) and *Archangelisa lemnis-cata* (Becc.) (Brooks, Philippine Journ. of Science, 1910, v, 442), *Xanthoxylum clava Herculis* (Chevallier and Pelletan, Journ. de Chim. Medicale, 1826, **2**, 314), yellow Assam wood or "Woodumpar" (Crookes' "Dyeing and Calico Printing"), *Phellodendron Amurense* (rind) (Shimo, Sci. Rep. Tohoku Imp. Univ. 1921, **10**, 331).

Oxyberberine has been isolated from *Berberis Thumbergii*, D. C. var. Maximowiczi, Franch. (Kondo and Tomita, Arch. Pharm. 1930, **268**, 549).

A. G. P. & E. J. C.

BARBITURIC ACID, *malonylurea*, 2:4:6-*trioxyhexahydropyrimidine*,



$$CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>CH_2$$

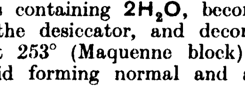
was first obtained by Baeyer (Annalen, 1863, **127**, 199; 1864, **130**, 136) by reducing with hydrogen iodide or sodium amalgam, the compound (*dibromobarbituric acid*) prepared by the action of bromine on violuric or dilituric acid. It can be prepared by the reducing action of warm concentrated sulphuric acid on alloxantin (Finck, *ibid.* 1864, **132**, 304); or synthetically by the condensation of ethyl sodiomalonate with urea in alcoholic solution (Michael, J. pr. Chem. 1887 [ii], **35**, 456). Barbituric acid has also been prepared by the action of hot mineral or acetic or formic acid on the iminobarbituric acid obtained by the condensation of urea with ethyl cyanacetate in the presence of sodium ethoxide (Conrad, Annalen, 1905, **340**, 310); or similarly from the *di-iminobarbituric acid* obtained from malononitrile and urea (Merck, G.P. 166448); or the *tri-iminobarbituric acid* obtained by the condensation of malononitrile with guanidine (Merck, G.P. 165692, 165693); or by the condensation of ethyl malonamate with urethane (Chemische Fabrik auf Aktien, vorm. E. Schering, G.P. 171294); or by the action of alkaline condensing agents on the ureides of the half-acid esters of malonic acid,

$$RO_2C{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$$

(Boehringer and Sohne, G.P. 193447); or by the action of ammonia on malonyl diurethane (Conrad and Schulze, Ber. 1909, **42**, 729).

It is most conveniently prepared in the laboratory by condensation of malonic acid with urea in the presence of phosphoryl chloride (Grimaux, Bull. Soc. chim. 1879 [ii], **31**, 146) or acetic anhydride (Biltz and Wittek, Ber. 1921, **54** [B], 1035).

Barbituric acid crystallises in large colourless prisms containing $2H_2O$, becomes anhydrous in the desiccator, and decomposes on melting at 253° (Maquenne block); it is a dibasic acid forming normal and acid salts, the acidic constant $ka = 10{\cdot}51 \times 10^{-5}$ (Wood, J.C.S. 1906, **89**, 1835), and the salts have the constitution represented by the formula



$$CO<\begin{matrix}NH{\cdot}C(OM)\\NH{\cdot}CO\text{——}\end{matrix}>CH$$

(Wood and Anderson, *ibid.* 1909, **95**, 979): the *ammonium* $C_4H_3O_3N_2(NH_4)$, *potassium* $C_4H_3O_3N_2K$, *sodium* $C_4H_3O_3N_2Na$, and $C_4H_2O_3N_2Na_2,2H_2O$, *barium*

$$(C_4H_3O_3N_2)_2Ba,2H_2O,$$

copper $(C_4H_3O_3N_2)Cu,3H_2O$, and *lead*

$$C_4H_2O_3N_2Pb,$$

salts are crystalline (Baeyer, Annalen, 1864, **130**, 141); *cf.* Biltz (Annalen, 1914, **404**, 186).

For morphine barbituric acids, useful as sedatives, *v.* B.P. 107409. Goméz (Anal. Fís. Quím. 1931, **29**, 280) has shown that the ultra-violet absorption spectrum of barbituric acid has a definite band at 2,500 Å.

Alkyl and Aryl Barbituric Acids.

These derivatives of barbituric acid fall into two main classes: (i) those substituted on the nitrogen atoms (the 1 and 3 positions), and (ii) those substituted on the 5-carbon atom.

(i) ***N*-Substituted Derivatives.**—These are generally prepared by condensation of the appropriate substituted urea with malonic acid. Among the better known are: 1-*Methyl-barbituric acid,*

$$\underline{\mathrm{NMe{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO}},$$

m.p. 133° (Conrad, Annalen, 1905, **340**, 310); 1 : 3-*dimethylbarbituric acid,* flattened needles (Mulder, Ber. 1879, **12**, 465; Techow, *ibid.* 1894, **27**, 3082); 1 : 3-*diethylbarbituric acid,* m.p. 52°–53° (Sembritzki, *ibid.* 1897, **30**, 1814); 1 : 3-*diphenyl,* m.p. 238° (Whiteley, J.C.S. 1907, **91**, 1339); 1-*phenyl-3-methyl,* m.p. 118°–120° (Hepner and Frenkenberg, Ber. 1932, **65** [B], 123).

(ii) ***C*-Substituted Derivatives.**—These have been prepared by very varied methods. Among these are (1) Direct alkylation of the barbituric acid by the action of the alkyl halide on the silver or sodium salt (Conrad and Guthzeit, Ber. 1881, **14**, 1643; 1882, **15**, 2844; Gebrüder von Niessen, G.P. 144432, 526390). (2) Condensation of the *ethyl ester* of the *alkyl malonic acid* with (*a*) *carbamide* in the presence of sodium ethoxide, the alkali metal or its amide (Merck, G.P. 146948, 147278, 147279, 147280; Fischer and Dilthey, Annalen, 1904, **335**, 334); (*b*) *biuret* or *alkyl allophanate* (Merck, G.P. 183857); (*c*) *carbamide* in the presence of alkali or alkaline earth carbides (Merck, G.P. 185963); (*d*) *guanidine* and subsequent hydrolysis of the 2-iminobarbituric acid obtained (Chemische Fabrik auf Aktien, vorm. E. Schering, G.P. 189076). (3) Condensation of *alkyl malonyl chloride* with (*a*) *carbamide* (Merck, G.P. 146949); (*b*) *guanidine* and subsequent hydrolysis with dilute acid of the 2-iminobarbituric acid obtained (Merck, G.P. 158890); (*c*) *urethane* and the conversion of the diurethanes into the barbituric acid by heating with alkyl oxides, hydroxides or fuming mineral acids (Traube, G.P. 171992, 172885, 172886); (*d*) with *alkyl allophanates* (Merck, G.P. 177694). (4) Condensation of the *alkyl malonitrile* with: (*a*) *guanidine* and subsequent hydrolysis of the 2 : 4 : 6-tri-iminobarbituric acid thus obtained (Merck, G.P. 165692, 165693); (*b*) *carbamide, thiocarbamide* or *guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, G.P. 185963). (5) Condensation of *dialkylmalonamides* with (*a*) *alkyl carbonates* in the presence of alkali ethoxides (Farbenfabriken vorm. Friedr. Bayer & Co., G.P. 163136, 168406, 168407); (*b*) *oxalyl chloride* (Einhorn, G.P. 225457). (6) By the action of acid condensing agents on the tetra-substituted diureides of the dialkylmalonic acids $\mathrm{CX_2(CO{\cdot}NH{\cdot}CO{\cdot}NR_2)_2}$ (Einhorn, G.P. 193446). (7) By the action of alkali condensing agents on the ureides of the half acid esters of alkylmalonic acids:

$$\mathrm{NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CRR'{\cdot}CO_2R''}$$

(Boehringer and Söhne, G.P. 193447). (8) Condensation of *ethyl dialkylcyanacetate* with: (*a*) *carbamide* in the presence of sodium ethoxide, and subsequent hydrolysis of the 4-iminobarbituric acid thus obtained (Merck, G.P. 156384, 156385); (*b*) *carbamide* or *thiocarbamide* and subsequent hydrolysis of the imino or thioiminobarbituric acid thus obtained by heating with mineral, formic, or acetic acids (Conrad, Annalen, 1905, **340**, 310); (*c*) *guanidine* in the presence of various condensing agents, and subsequent hydrolysis of the 2 : 4-di-iminobarbituric acid thus obtained (Farbenfabriken vorm. Friedr. Bayer & Co., G.P. 158502; Chemische Fabrik auf Aktien, vorm. E. Schering, G.P. 201244; Basler Chemische Fabrik, G.P. 204795); (*d*) *dicyanodiamides* in the presence of alkali condensing agents and subsequent hydrolysis of the substituted barbituric acid thus obtained (Farbenfabriken vorm. Friedr. Bayer & Co., G.P. 165223); (*e*) *carbamide, thiocarbamide,* or *guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, G.P. 185963).

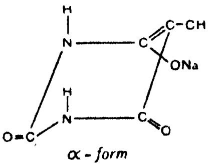
The following 5-alkyl derivatives have been described: 5-*methyl,** m.p. 202°–203° [1]; 5-*ethyl,* m.p. 194° [1, 2]; 5-*propyl,* m.p. 207°–208° [3]; 5-iso*propyl,* m.p. 216° [3]; 5-*allyl,* m.p. 167° [3]; 5-n-*butyl,* m.p. 210°–215° [9]; 5-sec-*butyl,* m.p. 199° [7]; 5 *amyl,* m.p. 215° [25]; 5-*hexyl,* m.p. 216° [16]; 5-cyclo*pentenyl,* m.p. 221°–223° [30, 31]; 5-cyclo*hexyl,* m.p. 254°–256° [7]; 5-*benzyl,* m.p. 206° [4]; 5-α-*furfuryl,* m.p 186°–188° [23, 28]; 5-*vanillal,* [40]; 5-α-*naphthylethyl,* m.p. 196°–198° [35].

The 5 : 5- disubstituted compounds have attracted great attention owing to their hypnotic properties. Dox and Yoder (J. Amer. Chem. Soc. 1922, **44**, 1141) and many others have shown that double alkyl substitution of the 5-carbon atom is essential for the product to have hypnotic properties. These conditions are further discussed by Dox (J. Amer. Pharm. Assoc. 1923, **12**, 602) and others.

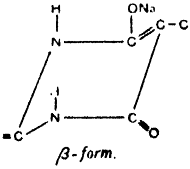
Among the very large number of these substances which have been prepared are the 5 : 5-*dimethyl,* m.p. 267° [1, 42]; 5-*methyl-5-ethyl,* m.p. 212° [1, 43]; 5-*methyl-5-propyl,* m.p. 182° [1]; 5-*methyl*-5-iso*propyl,* m.p. 186°–187° [12]; 5-

---

* Nishikawa (Mem. Ryojun Coll. Eng. 1931, **2**, 27) claims to have obtained two stereoisomeric forms of 5-methyl barbituric acid from the product of reaction between *iso*-succinic acid, and urea in the presence of sodium ethoxide. The α-form has m.p. 207° and the β-form 197°. The following formulæ are advanced (based on Wittig's theory of strainless rings) (Stereochemie, 1931, 141):



α-form



β-form

methyl-5-benzyl, m.p. 207°[5] ; 5 : *5-diethyl*, m.p. 191° (corr.)[1] ; (*see* VERONAL and SYNTHETIC DRUGS) ; *5-ethyl-5-propyl*, m.p. 146°[1, 41] ; *5-ethyl-5-butyl*, m.p. 125°–128°[6, 9, 15] ; *5-ethyl-5-*iso*butyl*, m.p. 174°–176°[9, 10] ; *5-ethyl*-5-sec-*butyl*, m.p. 84°–86°[14] ; 155°–157°[25] ; *5-ethyl-5-amyl*, m.p. 135°[25] ; *5-ethyl*-5-iso*amyl*, m.p. 154°–156°[9, 10] ; *5-ethyl-5-hexyl*, m.p. 112°–113°[16, 22] ; *5-ethyl-5-benzyl*, m.p. 206°–207°[5] ; *5-ethyl-5-phenylethyl*, m.p. 168°[18] ; *5-ethyl-5-*Δ^1-cyclo*pentenyl*, m.p. 182°–183°[27, 30] ; *5-ethyl-5-*Δ^2-cyclo*hexenyl*, m.p. 172°[27] ; *5-ethyl-5-α-naphthyl*, m.p. 254°–255°[35] ; *5-ethyl-5-α-furfuryl*, m.p. 144°–145°[28] ; 5 : *5-dipropyl*, m.p. 146°[1] ; 166°[41] (*see also* SYNTHETIC DRUGS) ; *5-propyl*-5-iso*propyl*, m.p. 161–162°[9] ; *5-propyl-5-butyl*, m.p. 153°[9] ; *5-propyl*-5-iso*butyl*, m.p. 164°–165°[9] ; *5-propyl-5-benzyl*, m.p. 210°[5] ; 5 : 5-*di*-iso*propyl*, m.p. 230°[12] ; 5-iso*propyl-5-butyl*, m.p. 209°–210°[9] ; 5-iso*propyl-5-allyl*, m.p. 137°–138°[8, 11, 12] ; 5-iso*propyl-5-propargyl*, m.p. 165°[26, 32] ; 5-iso*propyl-5-benzyl*, m.p. 229°[5] ; 5 : *5-diallyl*, m.p. 173°[3] ; 5 : 5-*di*-iso*butyl*, m.p. 173°–174°[1] ; *5-butyl-5-benzyl*, m.p. 195°[5] ; 5-iso*butyl-5-benzyl*, m.p. 255°[5] ; 5-sec-*butyl-5-allyl*, m.p. 110°[21, 34] ; 5-sec-*butyl-5-β-bromallyl*, m.p. 131°–132°[34] ; 5 : *5-diamyl*, m.p. 118°[25] ; 5 : 5-*di*-iso*amyl*, m.p. 172°[1] ; *5-crotyl-5-allyl*, m.p. 125°–126°[17, 29] ; dl-*5-ethyl*-5-sec-*octyl*, m.p. 126°–127°[24] ; 5 : *5-di-β-butenyl*, m.p. 108°[13] ; 5 : *5-dibenzyl*, m.p. 222°[1, 41].

Poly-Substituted Derivatives.—Among the more important poly-substituted derivatives are the following 1 : *3-dimethyl*-5-iso*butyl*, m.p. 195°–197°[19, 20] ; 1-*methyl*-5 : *5-diethyl*, m.p. 154°[1] ; 1-*phenyl*-5 : *5-diethyl*, m.p. 197°[1] ; 1 : 3 : 5 : 5-*tetraethyl*, b.p. 125·5°–126°/8 mm.[1] ; 1-p-*tolyl*-5 : *5-diethyl*, m.p. 152°–153° ; 1-p-*anisyl*-5 : *5-diethyl*, m.p. 126°–127° ; 1-p-*ethoxyphenyl*-5 : *5-diethyl*, m.p. 152°–153° ; 1-p-*chlorophenyl*-5 : *5-diethyl*, m.p. 135°–136° ; 1-p-*bromophenyl*-5 : *5-diethyl*, m.p. 186° ; 1-*phenyl-5-ethyl-5-propyl*, m.p. 152°–153° ; 1 : 3-*diphenyl-5-ethyl*, m.p. 145° (Hjort and Dox, J. Pharm. Exp. Ther. 1929, **35**, 155) ; 1-*benzyl*-5 : *5-diethyl*, m.p. 127° ; 1-*benzyl*-5 : *5-diallyl*, m.p. 116° ; 1-*benzyl-5-ethyl*-5-iso*amyl*, m.p. 90° ; 1-*benzyl-5-phenyl-5-ethyl*, m.p. 113° ; 1 : 3 : 5-*triallyl*, m.p. 68°–69° ; 1 : 3-*diallyl*-5 : 5-*dipropyl*, m.p. 62°–63° (Dox and Jones, J. Amer. Chem. Soc. 1929, **51**, 316) ; *5-ethyl-5-β-dimethylaminoethyl*, m.p. 171° ; *5-ethyl-5-β-diethylaminoethyl* (hydrochloride, m.p. 258°–260°) (Voorhees and Skinner, J. Amer. Chem. Soc. 1925, **47**, 1124) ; *di-β-bromallyl* (B.P. 223221) ; *di-β-brompropyl*, m.p. 237°–239°[44] ; 5-*β-hydroxyethyl*, m.p. above 300°[46] ; *5-phenyl-β-hydroxyethyl*, m.p. 200°[48] ; 5-o-*hydroxybenzylethyl*, m.p. 215°[47] ; 5-iso*propyl-5-methylol*, m.p. 195°–199°[49] ; *5-butyl-5-phenoxy*, m.p. 167°[45] ; 1-*β-phenylethyl*-5 : *5-diethyl* (Buck, J. Amer. Chem. Soc. 1934, **56**, 1607).

The following authors also give general methods of preparing alkyl barbituric acids with many examples. Tiffeneau and Sommaire (Bull. Soc. chim. 1923 [iv], **33**, 183, 189) ; Dox and Thomas (J. Amer. Chem. Soc. 1923, **45**, 1811) ; Volwiler (*ibid.* 1925, **47**, 2236) ; Hill and Keach (*ibid.* 1926, **48**, 257) ; Swiss P. 127126 ; Volwiler and Tabern (J. Amer. Chem. Soc. 1930, **52**, 1676) ; G.P. 526854 ; Rosenberg, Kneeland, and Skinner (J. Amer. Chem. Soc. 1934, **56**, 1339).

Thio-Barbituric Acids are described by Einhorn (Annalen, 1908, **359**, 145) and Merck (G.P. 234012).

[1] Fischer and Dilthey, Annalen, 1904, **335**, 334.

[2] G.P. 165693.

[3] Johnson and Hill, Amer. Chem. J. 1911, **46**, 537.

[4] Conrad and Guthzeit, Ber. 1882, **15**, 2,844.

[5] Dox and Yoder, J. Amer. Chem. Soc. 1922, **44**, 1141.

[6] *Idem.*, *ibid.*, p. 1578.

[7] *Idem.*, *ibid.*, p. 1564.

[8] B.P. 181347.

[9] Shoule and Moment, J. Amer. Chem. Soc. 1923, **45**, 243.

[10] U.S.P. 1514573.

[11] U.S.P. 1444802.

[12] Preiswerk, Helv. Chim. Acta, 1923, **6**, 192.

[13] Braun and Schirmacher, Ber. 1923, **56** [B], 538.

[14] U.S.P. 1478463.

[15] Tiffeneau, Bull. Sci. Pharmacol. 1924, **31**, 129.

[16] Dox, J. Amer. Chem. Soc. 1924, **46**, 1707.

[17] U.S.P. 1511919.

[18] Dox, J. Amer. Chem. Soc. 1924, **46**, 2843.

[19] Prusse, Annalen, 1925, **441**, 203.

[20] Behrend and Roosen, *ibid.* 1889, **251**, 235.

[21] U.S.P. 1615870.

[22] U.S.P. 1624546.

[23] Ojiyama, Hasegawa, and Matsumara, J. Pharm. Soc. Japan, 1926, No. 533, 597.

[24] Hsueh and Marvel, J. Amer. Chem. Soc. 1928, **50**, 855.

[25] Dox and Jones, *ibid.*, p. 2033.

[26] U.S.P. 1682062.

[27] U.S.P. 1690796.

[28] Kriner and Richter, J. Amer. Chem. Soc. 1929, **51**, 3181.

[29] G.P. 489251.

[30] Shoule, Keltch, and Swanson, J. Amer. Chem. Soc. 1930, **52**, 2440.

[31] F.P. 684111.

[32] G.P. 526390.

[33] Fourneau, J. Pharm. Chim. 1931, **14**, 513.

[34] G.P. 575470.

[35] Keach, J. Amer. Chem. Soc. 1933, **55**, 2975.

[36] Shoule and Waldo, *ibid.* p. 4649.

[37] Hooper and Johnson, *ibid.* 1934, **56**, 484.

[38] G.P. 487192.

[39] Buck, J. Amer. Chem. Soc. 1934, **56**, 1607.

[40] Kataoka, J. Biochem. Japan, 1934, **19**, 11.

[41] Conrad, Annalen, 1905, **340**, 310.

[42] G.P. 180669.

[43] G.P. 144432.

[44] Staudinger, Chem. Zentr. 1923, ii, 748.

[45] Dox and Yoder, J. Amer. Chem. Soc. 1922, **44**, 1578.

[46] Cretcher, Koch, and Pittenger, *ibid.* 1925, **47**, 3083.

[47] Ojiyama, *et al.*, *cf.* [23].

[48] Nelson and Cretcher, J. Amer. Chem. Soc. 1928, **50**, 2758.

[49] Swiss P. 163698.

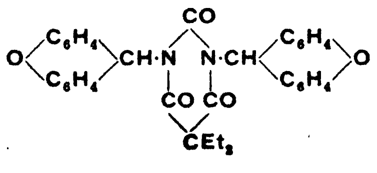
Substituted barbituric acids are employed in pharmacy under the following trade names :

Allonal (numal) .	5-*iso*propyl-5-allyl.
Amytal . . .	5-ethyl-5-*iso*amyl.
Dial	5 : 5-diallyl.
Dibromin . . .	5 : 5-dibromodiallyl.
Evipan . . .	1-methyl-5-methyl-5-*cyclo*hexenyl (sodium salt).
Ipral	5-ethyl-5-*iso*propyl (calcium salt).
Medinal . . .	5 : 5-diethyl (sodium salt).
Nembutal . . .	5-ethyl - 5 - α - methylbutyl (sodium salt).
Neonal (soneryl) .	5-ethyl-5-butyl.
Noctal . . .	5-β-bromoallyl-5-*iso*propyl (or 5-*iso*butyl-5-brompropenyl).
Pentenal . . .	5-*cyclo*pentenyl-5-ethyl.
Pentobarbital .	5-ethyl-5-α-methylbutyl.
Pernocton . .	5-β-bromallyl-5-*sec.*-butyl.
Phanodorm . .	5-ethyl-5-Δ^2-*cyclo*hexenyl.
Phenobarbital (luminal or gardénal) . . .	5-ethyl-5-phenyl.
Prominal . . .	1-methyl-5-ethyl-5-phenyl
Proponal . . .	5 : 5-dipropyl.
Rectidon . . .	5-β-bromallyl-5-α-methylbutyl.
Rutonal . . .	5-methyl-5-phenyl.
Sandoptal . . .	5-allyl-5-*iso*butyl.
Veronal (barbital)	5 : 5-diethyl.

The pharmacological and physiological properties of substituted barbituric acids are the subject of a very extensive literature which cannot be conveniently summarised in this article ; reference should be made to: Carnot and Tiffeneau (Compt. rend. 1922, **175**, 241) ; Dox and Hjort (J. Pharm. Exp. Ther. 1927, **31**, 455 ; 1929, **35**, 155) ; Vogt (Arch. exp. Path. Pharm. 1930, **152**, 341) ; Boedecker and Ludwig (*ibid.* 1929, **139**, 353) ; Shoule and Moment (J. Amer. Chem. Soc. 1923, **45**, 243) ; Redonnet (Compt. rend. Soc. Biol. 1924, **91**, 808) ; Nielsen, Higgins, and Spruth (J. Pharmacol. 1925, **26**, 371) ; Henriksen (Pharm. J. 1934, **132**, 200).

Other derivatives are used in pharmacy for various purposes, these include the quinine salts, complex compounds with pyrazolones and similar compounds. The work on these substances is very extensive and the references (usually to Patents) are readily found in the indexes to the British or American chemical abstracts.

Identification of Barbituric Acids.—Fabre (J. Pharm. Chim. 1922 [vii], **26**, 241 ; Bull. Soc. chim. 1923 [iv], **33**, 791) proposes to use, for purposes of identification, the melting points of the crystalline dixanthyl derivatives formed by heating the disubstituted acid with xanthydrol at 100° for 1 minute. The test can be carried out on 0·01 g. The derivative of *veronal*



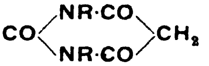
melts at 245°–246° ; of *phenobarbital* at 218°–219° while that of *dial* has m.p. 242°–243°. This test supplements the microchemical tests of van Itallie and Van der Veen (J. Pharm. Chim. 1918 [vii], **22**, 243). Parri (Boll. Chim. farm. 1924, **63**, 401) describes a colour reaction for *veronal* with phenylhydrazine, sodium nitroprusside, an alkaline solution of cobalt salt, and a solution of α-naphthol in sulphuric acid. Barbituric acid gives a red colour with alkaline solutions of picric acid which is not obtained with the dialkyl derivatives (Dox, Z. physiol. Chem. 1925, **150**, 118 ; Greenwald, J. Amer. Chem. Soc. 1928, **50**, 1469). Lyons and Dox have described the 1-*p*-nitrobenzyl compound, m.p. 192° (J. Amer. Chem. Soc. 1929, **51**, 288). *Dial* gives a cherry red coloration when warmed with a 1% solution of vanillin in sulphuric acid (Lagarge, J. Pharm. Chim. 1930 [viii], **12**, 364). *Barbital* gives an emerald green colour with selenious acid and sulphuric acid, while *phenobarbital* yields a wine-red coloration (Ekkert, Amer. Chem. Abstr. 1932, **26**, 5380). Hargreaves and Nixon (J. Amer. Pharm. Assoc. 1933, **22**, 1250) give a useful summary of simple tests for nine derivatives.

Further tests are described by van Itallie and Steenhauer (Pharm. Weekblad, 1930, **67**, 977); Deniges (Bull. Soc. Pharm. Bordeaux, 1929, **67**, 165) ; Zamparo (Boll. Chim. farm. 1925, **64**, 257); Ekkert (Pharm. Zentr. 1926, **67**, 481) ; Vitte (Bull. Soc. Chim. biol. 1930, **12**, 524); Kaiser (Suddeutsche Apoth.-Ztg. 1930, **70**, 339 ; 1931, **71**, 518 ; 1932, **72**, 57, 65) ; Deniges (Microchemie, 1931, **3**, 316) ; David (Pharm.-Ztg. 1932, **77**, 1165) and many others.

Buddle (Apoth.-Ztg. 1924, **49**, 295) proposes to *estimate* barbituric acids by dissolving a weighed sample in aqueous sodium carbonate and titrating with 0·1*N* silver nitrate until turbidity just persists.

Ether-like derivatives of barbituric acid, prepared by the usual methods from aryl- or alkyl-aryloxyalkyl malonic acid, containing at least one aryl residue attached to an oxygen atom, possess strong hypnotic action combined with low toxic effects, Farbenfabriken vorm. F. Bayer & Co., G.P. 295492, from J.S.C.I. 1917, **36**, 306.

The methylene group situated between two CO groups in barbituric acid and in its 1- and 1 : 3-substituted derivatives



$$CO\begin{matrix}\diagup NR\cdot CO \diagdown \\ \diagdown NR\cdot CO \diagup\end{matrix}CH_2$$

is highly reactive, and the hydrogen atoms can be replaced by: (1) acyl groups forming the *acyl barbituric acids* (*v. infra*) ; (2) halogens yielding the halogen derivatives of barbituric acid (*v. infra*) ; (3) hydroxyl yielding the *dialuric acids* $CO[NR\cdot CO]_2CH\cdot OH$ and the *alloxans* $CO[NR\cdot CO]_2C(OH)_2$ or

$$CO[NR\cdot CO]_2CO$$

(*q.v.*) ; (4) a nitro group, yielding the *dilituric acids* $CO[NR\cdot CO]_2CH\cdot NO_2$ (*q.v.*) ; (5) a *nitroso group* forming the *isonitroso barbituric acids* or *violuric acids* $CO[NR\cdot CO]_2C : NOH$ (*v. infra*) ; (6) the amino group yielding the *uramil* (*murexan*) $\mathrm{CO[NR{\cdot}CO]_2CH{\cdot}NH_2}$ (*v. infra*), of which the sulphamino derivative is *thionuric acid*,

$$\mathrm{CO[NR{\cdot}CO]_2CH{\cdot}NH{\cdot}SO_3H}$$

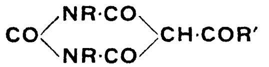
(*v. infra*), and the carbamido derivative is *ψ-uric acid* $\mathrm{CO[NR{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2}$ (*v. infra*); (7) alkyl groups, forming the 5- or C-*mono*-, and 5 : 5- or CC-*di-alkylbarbituric acids*

$$\mathrm{CO[NR{\cdot}CO]_2CHR'}$$

and $\mathrm{CO[NR{\cdot}CO]_2CR'R''}$ (*v. supra*).

Barbituric acid and its 1- or 1 : 3- substituted derivatives also condense with aldehydes to form derivatives of the type $\mathrm{CO[NR{\cdot}CO]_2C : CHR'}$ (*v. infra*), and with aromatic diazonium salts to form *hydrazones* $\mathrm{CO[NR{\cdot}CO]_2C : N{\cdot}NHR'}$, and *azo* compounds $\mathrm{CO[NR{\cdot}CO]_2CR'N : NR''}$ (*v.* ALLOXAN, and *infra*).

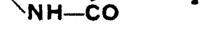
Acyl derivatives of barbituric acid.—The acyl derivatives of barbituric acid and its 1 : 3-substituted derivatives are ketones of the type



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NR{\cdot}CO}\\ \mathrm{NR{\cdot}CO}\end{matrix}\right\rangle\mathrm{CH{\cdot}COR'}$$

and yield *oximes* and *hydrazones* (Biltz and Wittek, Ber. 1921, **54** [B], 1035). These acetyl derivatives occur as by-products in the synthetic formation of the acid from malonic acid and the carbamide in the presence of phosphoryl chloride. 5-*Acetylbarbituric acid* forms colourless crystalline needles, m.p. 296°–300° (decomp.) (Grimaux, Compt. rend. 1878, **87**, 752 ; 1879, **88**, 85 ; Conrad and Guthzeit, Ber. 1882, **15**, 2844 ; Biltz and Wittek, *l.c.*) ; 5-*acetyl*-1-*methylbarbituric acid*, m.p. 207° (decomp.) ; 5-*acetyl*-1 : 3-*dimethylbarbituric acid*, m.p. 195° ; 5-*acetyl*-1-*ethyl-barbituric acid*, m.p. 162°–163° ; *Biltz* and Wittek (*l.c.*) ; 1 : 3-*diethylacetylbarbituric acid* $\mathrm{C_8H_4N_2O_3Ac}$ has m.p. 62·5° (Sembritzki, Ber. 1897, **30**, 1814) ; 1 : 3-*diphenylacetylbarbituric acid* $\mathrm{C_{16}H_{11}O_3N_2Ac}$, obtained as a by-product in the synthetic preparation 1 : 3-diphenylbarbituric acid, also prepared by the action of acetyl chloride on sodium 1 : 3-diphenylbarbiturate, has m.p. 150°, and forms a sparingly soluble sodium salt ; 1 : 3-*diphenyl-5-ethylacetylbarbituric acid*, obtained by the action of ethyl iodide and silver oxide on the preceding compound, has m.p. 139°. 1 : 3-*Diphenylbenzoylbarbituric acid* $\mathrm{C_{16}H_{11}O_3N_2Bz}$ prepared from benzoyl chloride and sodium 1 : 3-diphenylbarbiturate has m.p. 228° ; the 5-*methyl* derivative has m.p. 158°, the 5-*ethyl* derivative has m.p. 243°, and the 5-*bromo* derivative melts at 186°, and is reduced to the benzoyl compound by hydrogen iodide with the liberation of one molecular proportion of iodine (Whiteley and Judd, private communication ; Backes, West, and Whiteley, J.C.S. 1921, **119**, 378). 5-*Benzoylbarbituric acid* has been prepared by Biltz and Köhler (Ber. 1923, **56** [B], 5482) ; it has m.p. 275°.

Barbituryl-5-acetic acid



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}\right\rangle\mathrm{CH{\cdot}CH_2COOH}$$

chars at 230° and decomposes at 250° (Johnson and Kohmann, Amer. Chem. J. 1913, **49**, 192).

Acetonyl barbituric acids.—Barbituric acids condense readily with monochloroacetone, yielding acetonylbarbituric acids (Dox and Houston, J. Amer. Chem. Soc. 1924, **46**, 252) 5-*acetonyl*, m.p. 238°–240° (decomp.) ; 5 : 5-*diacetonyl*, m.p. 264°–266° (decomp.), etc.

Halogen derivatives of barbituric acid.—*Bromo derivatives.*—The 5-mono- and 5 : 5-dibromo derivatives of barbituric acid and its 1 : 3-substituted derivatives are reduced by hydrogen iodide, forming the corresponding barbituric acid, and liberating iodine according to the equation

$$\mathrm{CO[NR{\cdot}CO]_2CBr_2{+}4HI} \\ \mathrm{=CO[NR{\cdot}CO]_2CH_2{+}2HBr{+}2I_2}$$

the reaction is quantitative, takes place rapidly at the ordinary temperature, and affords a ready method of analysis (Backes, West, and Whiteley, *l.c.*).

5-*Bromobarbituric acid* $\mathrm{CO[NH{\cdot}CO]_2CHBr}$, prepared by reducing the dibromo derivative with sodium amalgam or zinc-dust, or by heating it with aqueous prussic acid, forms small needles, sparingly soluble in water (Baeyer, Annalen, 1864, **130**, 134). 5-*Bromobarbituric acid*, $\mathrm{CO[NH{\cdot}CO]_2CHBr{\cdot}2H_2O}$, prepared by treating 5 : 5-dibromobarbituric acid with concentrated ammonia solution, transforming the ammonium monobrombarbiturate into the sodium salt and boiling this with 40% sulphuric acid, has m.p. 210°–216° (decomp.) (Biltz and Hamburger, Ber. 1916, **49**, 635). It has also been obtained by treating barbituric acid with aqueous bromine at 50°–60° (Bock, Ber. 1922, **55** [B], 3400). 1-*Phenyl-5-bromo barbituric acid* is obtained by direct bromination (Voorhees and Skinner, J. Amer. Chem. Soc. 1925, **47**, 1124 ; Macbeth, J.C.S. 1926, 1253). 5 : 5-*Dibromobarbituric acid* $\mathrm{CO[NH{\cdot}CO]_2CBr_2}$, prepared by the action of bromine on barbituric, violuric, dilituric, or hydurilic acid (Baeyer, Annalen, 1863, **127**, 229), or by oxidising dibromooxymethyluracil with fuming nitric acid (Behrend, *ibid.* 1886, **236**, 62), forms sparingly soluble rhombic crystals, m.p. 234° (decomp.). 5-*Bromo-5-methylbarbituric acid* has m.p. 192·5° (corr.) (Fischer and Dilthey, *ibid.* 1904, **335**, 334). 1-*Methyl-5-bromo-barbituric acid*, m.p. 105°–106°. 1-*Methyl*-5 : 5-*dibromo-barbituric acid*, m.p. 98°–99° (Biltz and Hamburger, Ber. 1916, **49**, 635).

1 : 3-*Diethyl-5-bromo-barbituric acid*, m.p. 81°–82° (Biltz and Hamburger, *l.c.*). 1 : 3-*Diethyl*-5 : 5-*dibromobarbituric acid*,

$$\mathrm{CO[NEt{\cdot}CO]_2CBr_2},$$

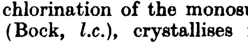
has m.p. 86°–87° (corr.) (Sembritzki, Ber. 1897, **30**, 1814). 1 : 3-*Diphenyl-5-bromobarbituric acid* $\mathrm{CO[NPh{\cdot}CO]_2CHBr}$ has m.p. 155° (Backes, West, and Whiteley, *l.c.*). 1 : 3-*Diphenyl*-5 : 5-*dibromobarbituric acid*,

$$\mathrm{CO[NPh{\cdot}CO]CBr_2,C_6H_6},$$

m.p. 152° ; the benzene-free compound has m.p. 160° (Whiteley, J.C.S. 1907, **91**, 1347) ; 5-*bromo*-1 : 3-*diphenyl-5-benzoylbarbituric acid* has m.p. 186° (Whiteley, Chem. Soc. Proc. 1908, **24**, 288).

Chloro derivatives.—*5-Chlorobarbituric acid* decomposes at 280° (Biltz and Hamburger, *l.c.*). It may be obtained by direct chlorination of barbituric acid, or by heating the 5-bromo compound for a few minutes with fuming hydrochloric acid (Bock, Ber. 1923, **56** [B], 1222). 5 : *5-Dichlorobarbituric acid*, obtained by the oxidation of dichloro-oxymethyluracil, or by further chlorination of the monosubstituted compound (Bock, *l.c.*), crystallises in prisms or plates, $a : b : c = 0·7766 : 1 : 0·8929$ (Behrend, Annalen, 1886, **236**, 57), m.p. 219°–220° (Biltz and Hamburger, *l.c.*). *5-Chloro-1-methylbarbituric acid* crystallises in quadratic tables with one molecule of water, m.p. 137°. *5-Chloro-1 : 3-dimethylbarbituric acid* crystallises with one molecule of water, m.p. 129° (Biltz and Hamburger, *l.c.*). 5 : *5-Dichloro-1 : 3-dimethylbarbituric acid*, obtained by treating amalic acid (tetramethylalloxantin) with phosphoryl chloride, has m.p. 157° (Techow, Ber. 1894, **27**, 3082). 5 : *5-Dichloro-1 : 3-diethylbarbituric acid* has m.p. 85·7 (corr.) (Sembritzki, *ibid.* 1897, **30**, 1814). Nightingale and Schaeffer (J. Amer. Chem. Soc. 1932, **54**, 236) describe the reaction of the 5 : 5-dibromo compound with ethylamine to form 5-bromo-7-ethyl uramil, but Cope (*ibid.* p. 1250) prefers to regard it as an alkyl ammonium salt of 5-bromobarbituric acid.

Dialuric acid, *Hydroxybarbituric acid*, *Tartronylurea*,

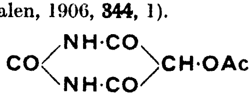


$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\!>\!\mathrm{CH\cdot OH}$$

prepared by reducing alloxan with zinc and hydrochloric acid, or with sulphuretted hydrogen at the temperature of boiling water (Liebig and Wöhler, Annalen, 1838, **26**, 276), or with ammonium sulphide, when ammonium dialurate is obtained and is readily converted into the acid by the action of hot dilute hydrochloric acid (Gregory, Chem. Soc. Mem. 1845, **2**, 11). A mixture of potassium dialurate and oxalurate is obtained by adding potassium carbonate to a solution of alloxan containing potassium cyanide (Strecker, Annalen, 1860, **113**, 53) ; it is prepared by reducing alloxantin with sodium amalgam, or dibromobarbituric acid with sulphuretted hydrogen (Baeyer, Annalen, 1863, **127**, 12 ; 1864, **130**, 133). Magnier de la Source showed that dialuric acid is obtained by prolonged boiling of uric acid with water (Bull. Soc. chim. 1875, **23**, 529), or it can be obtained from uric acid on gentle heating with hydrochloric acid and potassium chlorate (Biltz and Damm, Ber. 1913, **46**, 3662). Grimaux effected its synthesis by treating tartronic acid and urea with phosphoryl chloride (Compt. rend. 1879, **88**, 85).

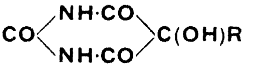
Dialuric acid forms colourless short four-sided prisms, or narrow thin leaflets with rounded ends, sparingly soluble in cold, more readily so in hot water ; turns red at 180°, m.p. 214°–215° (corr.) (Biltz and Damm, *l.c.*, p. 3664). The moist crystals or the aqueous solution rapidly absorbs oxygen from the air to form alloxan, which combines with the dialuric acid, forming alloxantin. The rate at which the change takes place is illustrated by the results obtained by Hartley (J.C.S. 1905, **87**, 1804), in an unsuccessfu attempt to obtain the absorption spectra of dialuric acid ; pure dialuric acid was dissolved in water, and immediately afterwards the solution yielded the same series of absorption spectra as a solution of alloxantin. Alloxantin is also formed by mixing solutions of equivalent quantities of dialuric acid and of alloxan (*cf.* Richter, Ber. 1911, **44**, 2155). Dialuric acid is monobasic, and, contrary to the statements of Menschutkin (Ber. 1875, **8**, 760 ; Annalen, 1876, **182**, 70), forms only one series of salts of the type, $C_4H_3O_4N_2M'$. The *sodium*, *potassium*, *ammonium*, and *barium* salts are crystalline (Koech, Annalen, 1901, **315**, 246 ; Behrend and Friederich, Annalen, 1906, **344**, 1).

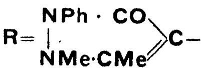
Acetyldialuric acid



$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\!>\!\mathrm{CH\cdot OAc}$$

crystallises in white prisms or leaflets; m.p. 210°–212°; gives a violet precipitate with barium hydroxide ; forms the *potassium salt* $C_6H_5O_5N_2K,H_2O$, and combines with alloxan to form *acetylalloxantin* $C_{10}H_8O_9N_4,H_2O$, m.p. 263°–265° ; *benzoyldialuric acid* $C_{11}H_8O_5N_2$, crystallises in prisms, m.p. 209°–210°, yields with barium hydroxide a white precipitate, turning violet, and combines with alloxan to form *benzoylalloxantin* $C_{15}H_{10}O_9N_4,H_2O$, or $1\frac{1}{2}H_2O$, m.p. 253°–255° (Behrend and Friederich, Annalen, 1906, **344**, 1). Brom-methyl barbituric acid treated with silver acetate yields *acetylmethyl*-dialuric acid, m.p. 244°–245° (Johnson, Baudisch and Hoffmann, J. Amer. Chem. Soc. 1932, **54**, 1106).





Substituted dialuric acids of the type $\mathrm{CO}\!<\!\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\!>\!\mathrm{C(OH)R}$ are obtained by the condensation of alloxan with (1) aromatic ketones, *e.g.* phenacyldialuric acid, where $R=C_6H_5\cdot CO\cdot CH_2-$; (2) aromatic amines, *e.g.* *p*-aminophenyltartronylurea, where

$$R=NH_2\cdot C_6H_4- ;$$

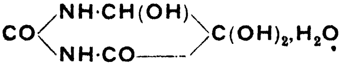
(3) pyrazolone bases, *e.g.* phenylmethylpyrazolonetartronylurea, where $R=\left|\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{NMe\cdot CMe}\end{matrix}\right\rangle\mathrm{C}-$; (4) phenols, *e.g.* *p*-hydroxyphenyltartronylurea, where $R=OH\cdot C_6H_4-$. For the preparation and technical application of these compounds, *see* art. ALLOXAN.

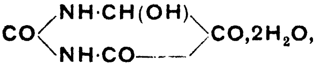
1-*Methyldialuric acid* $C_5H_6O_4N_2\cdot H_2O$, prepared by reducing dimethyl alloxantin with sodium amalgam, crystallises in round clusters of silky needles or narrow lancet-shaped leaflets, m.p. 167°–168° (corr.), or prepared directly from theobromine by careful treatment with finely divided potassium chlorate in presence of hydrochloric acid, crystallises in bundles of colourless glistening filaments, many of which widen to slender narrow leaflets. The molecule of water is driven off at 110°–120°. From alcohol the acid crystallises in anhydrous, stout, lustrous rhombohedra, m.p. 184°–185° (Biltz and Damm, Ber. 1913, **46**, 3665).

1 : 3-*Dimethyldialuric acid*, obtained by reducing amalic acid (tetramethyl-alloxantin) with sulphuretted hydrogen (Maly and Andreasch, Monatsh. 1882, **3**, 92), or with sodium amalgam (Techow, Ber. 1894, **27**, 3082), forms colourless compact crystals which become red at 100° and decompose at 170° (cf. Biltz and Damm, *ibid.* 3667) ; the acid crystallises with one molecule of water, which is partly lost in vacuum and completely at 110°. The hydrated acid has m.p. just under 100°, and begins to discolour at 190°, and has m.p. 218° (corr.) with decomposition. It forms crystalline alkali salts, and reduces cold solutions of silver and copper salts.

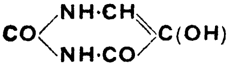
Oxidation of 5-ethylbarbituric acid with aqueous potassium dichromate yields 5-*ethyldialuric acid*, m.p. 216°–217°, which is not reduced by zinc and hydrochloric acid or zinc and acetic acid, but which, on treatment with alkali, yields ethyltartronic acid. The 5-*benzyl*- derivative has been similarly obtained, m.p. 214°–215° ($+2H_2O$) (Aspelund, J. pr. Chem. 1933 [ii], **136**, 329).

iso-Dialuric acid,


$$CO\left\langle\begin{matrix}NH\cdot CH(OH)\\NH\cdot CO\end{matrix}\right\rangle C(OH)_2,H_2O$$ (I)

or

$$CO\left\langle\begin{matrix}NH\cdot CH(OH)\\NH\cdot CO\end{matrix}\right\rangle CO,2H_2O,$$ (II)

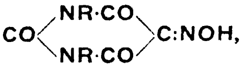
obtained by the action of bromine water on *iso*barbituric acid


$$CO\left\langle\begin{matrix}NH\cdot CH\\NH\cdot CO\end{matrix}\right\rangle C(OH)$$

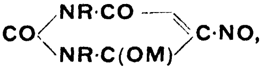
or aminouracil or hydroxyxanthine (Behrend and Roosen, Ber. 1888, **21**, 999), crystallises in trimetric prisms sometimes a centimetre long (Weinschenk, Annalen, 1889, **251**, 243), is readily soluble in water, less so in alcohol; it loses one molecule of water of crystallisation at 100°. The other molecule, which is regarded as water of constitution, is lost at 140°–150°, at which temperature the compound decomposes. Biltz and Paetzold (Annalen, 1927, **452**, 67) describe *iso*dialuric acid monohydrate, m.p. 133° (decomp.) with resinification at 180°, and further decomposition at 250° ; anhydrous *iso*dialuric acid melts at 190°. It is therefore concluded that *iso*dialuric acid has the formula I (above). *Iso*dialuric acid is converted into dialuric acid by the action of bases (Koech, Annalen, 1901, **315**, 246). It yields uric acid on condensation with urea, reduces solutions of silver salts, and combines with hydroxylamine to form two isomeric *oximino*- compounds. The α-oxime forms shining plates or prisms, becomes red and decomposes at 100° ; the β-oxime crystallises in needles which do not become red at 110° (Behrend and Roosen, Annalen, 1889, **251**, 244).

1-Methyl*iso*dialuric acid, $C_5H_8O_5N_2$, prepared by oxidising methyl*iso*barbituric acid (Lehmann, Annalen, 1889, **253**, 80) with bromine water, crystallises in rosette-like aggregates from water, and in contradistinction to *iso*dialuric acid, contains only 1 molecule of water, which is regarded as water of constitution.

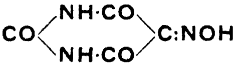
***iso*Nitroso derivatives of barbituric acids. Violuric acids.** Violuric acid or *iso*nitrosobarbituric acid is so called because, although colourless in the solid state, and forming colourless alkyl ethers, it shows a violet colour in solution in pure water, and gives rise to intensely coloured (red, violet, blue, green, and yellow) salts with metals and substituted ammonias (Wagner, Z. physikal. Chem. 1896, **12**, 314; Guinchard, Ber. 1899, **32**, 1723 ; Donnan and Schneider, J.C.S. 1909, **95**, 956 ; Zerewitinoff, Ber. 1909, **42**, 4802). Hantzsch and his pupils have shown that polychromatism and chromotropism are exhibited by some of the violurates, and they are of the opinion that the violuric acids and their colourless ethers are the true oximino ketones,


$$CO\left\langle\begin{matrix}NR\cdot CO\\NR\cdot CO\end{matrix}\right\rangle C{:}NOH,$$

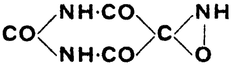
whilst the *blue* violurates are the nitroso-enolic salts,


$$CO\left\langle\begin{matrix}NR\cdot CO\\NR\cdot C(OM)\end{matrix}\right\rangle C\cdot NO,$$

and the more positive the nature of the metallic radicle present and the solvent, the more completely are the violuric acids as true oximinoketones transformed into the structurally isomeric nitroso-enols (Ber. 1899, **32**, 575 ; Guinchard, *ibid.* 1723 ; 1909, **42**, 966, 986, 1000 ; 1910, **43**, 45, 82). Another explanation of the differences in constitution between the colourless violuric acids and the coloured violurates is to regard the latter as derivatives of the oxime

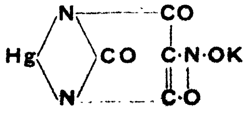

$$CO\left\langle\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right\rangle C{:}NOH$$

whilst the colourless acids are *iso*-oximes


$$CO\left\langle\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right\rangle C\left\langle\begin{matrix}NH\\|\\O\end{matrix}\right.$$

(Lowry, Brit. Assoc. Reports, 1904, 222; Hartley, J.C.S. 1905, **87**, 1816 ; Baly, *ibid.* 1906, **89**, 981 ; Whiteley, *ibid.* 1907, **91**, 1331).

Violuric acid $CO[NH\cdot CO]_2C{:}NOH,H_2O$, prepared by the action of nitrous acid or nitric acid (sp.gr. 1·2) on hydurilic acid (Baeyer, Annalen, 1863, **127**, 200) ; by treating barbituric acid with potassium nitrite (Baeyer, *ibid.* 1864, **130**, 140) ; by heating dilituric acid with glycerol, or by warming its iron salt with potassium cyanide ; or by the action of hydroxylamine hydrochloride on alloxan (Ceresole, Ber. 1883, **16**, 1133 ; Pellizzari, Gazzetta, 1887, **17**, 258), is a monobasic acid, and decomposes acetates ; it also yields a pale flesh-coloured *mercuric* derivative, the potassium salt



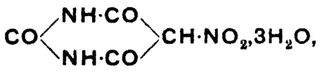
of which is deep violet, becoming blue when anhydrous (Auld, J.C.S. 1907, **91**, 1047). The *methyl ether* $C_4H_2O_3N_3{\cdot}CH_3$ is colourless, and has m.p. 270° (Guinchard, Ber. 1899, **32**, 1723); the *benzyl ether* $C_4H_2O_3N_3{\cdot}C_7H_7$ is also colourless, and has m.p. 222° (Hantzsch and Isherwood, *ibid.* 1909, **42**, 986).

1-*Methylvioluric acid*, $C_5H_5O_4N_3,H_2O$, decomposes carbonates and acetates (Andreasch, Monatsh. 1900, **21**, 281); it has m.p. 202°–203° (Biltz and Hamburger, *l.c.*). 1 : 3-*Dimethylvioluric acid* $CO[NMe{\cdot}CO]_2C{:}N{\cdot}OH,H_2O$ has m.p. 124°, the anhydrous substance melts at 141° (Techow, Ber. 1894, **27**, 3084; Andreasch, Monatsh. 1895, **16**, 17; Whiteley, J.C.S. 1903, **83**, 19); the benzyl ether $C_{13}H_{13}O_4N_3$ has m.p. 164° (Hantzsch and Isherwood, *l.c.*). 1 : 3-*Diethylvioluric acid*,

$$CO[NEt{\cdot}CO]_2C{:}NOH,H_2O,$$

melts at 90° and loses H_2O at 107° (Sembritzki, Ber. 1897, **30**, 1814). 1 : 3-*Diphenylvioluric acid* $CO[NPh{\cdot}CO]_2C{:}N{\cdot}OH$ has m.p. 227°; the *acetyl* derivative $C_{16}H_{10}O_4N_3Ac$, melts and decomposes at 245° (Whiteley, J.C.S. 1907, **91**, 1339). The colour and spectra of organic salts of violuric acid have been examined by Ghatak and Dutt (J. Indian Chem. Soc. 1928, **5**, 665), while Lifschitz and Hepner (Ber. 1922, **55** [B], 1619) have studied salt formation and colour-isomerism in the amino-violuric acids.

Dilituric acid, *5-nitrobarbituric acid, nitromalonylurea,*



$$CO\left\langle\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right\rangle CH{\cdot}NO_2,3H_2O,$$

obtained by treating alloxantin first with hydrochloric acid and subsequently with nitric acid (Schlieper, Annalen, 1845, **56**, 24); by warming hydurilic acid with nitric acid (Baeyer, *ibid.* 1863, **127**, 211); by nitrating barbituric acid with fuming nitric acid (Baeyer, *ibid.* 1864, **130**, 140); by oxidising violuric acid (nitrosobarbituric acid) (Ceresole, Ber. 1883, **16**, 1134); or by oxidising with nitric acid the compound

$$C_{16}H_{28}O_{11}N_{12}S_2$$

obtained by condensing *iso*dialuric acid with thiocarbamide (*v.* Vogel, Annalen, 1901, **315**, 259; Bartling, *ibid.* 1905, **339**, 27); it has also been prepared from violuric acid and nitric acid (Biltz and Sedlatscheck, Ber. 1924, **57** [B], 339) and by direct nitration of barbituric acid with fuming nitric acid below 40° (Hartmann and Sheppard, "Organic Syntheses," 1932, XII, 58).

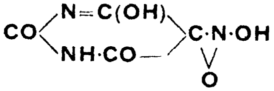
Dilituric acid, m.p. 180°–181°, crystallises in colourless quadratic prisms or plates, is sparingly soluble in cold, more readily so in hot water, is sparingly soluble in alcohol and insoluble in ether. It forms chloropicrin when warmed with bleaching powder, is reduced by hydriodic acid or tin and hydrochloric acid to *uramil* (*aminobarbituric acid*) (*see* below), and suffers partial reduction when heated with glycerol, yielding *violuric acid*. Dilituric acid is tribasic, but most of the salts are acidic, and contain only one equivalent of the metal; they are sparingly soluble in water, and are not generally decomposed by mineral acids. The *ammonium salt*

$$C_4H_2(NH_4)O_5N_3,$$

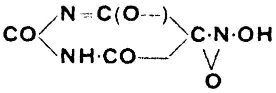
the *sodium salt* $C_4N_2NaO_5N_3,4H_2O$, *potassium salt* $C_4H_2KO_5N_3$, *calcium salt*

$$Ca(C_4H_2O_5N_3)_2,4H_2O,$$

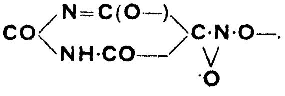
the *barium compound* $BaCl(C_4H_3O_5N_3),H_2O$, *ferrous salt* $Fe(C_4H_2O_5N_3)_2,8H_2O$, and the *silver salt* $C_4H_2AgO_5N_3,2H_2O$, are colourless; the *ferric salt* $Fe(C_4H_2O_5N_3)_3,6H_2O$ is bright yellow, the *copper salt* $Cu(C_4H_2O_5N_3),H_2O$ is greenish, the *dipotassium salt* $C_4HK_2O_5N_3$ is bright yellow (Schlieper, *l.c.*), and the *triargentic salt* $C_4Ag_3O_5N_3$ is lemon-yellow (Baeyer, Annalen, 1864, **130**, 140). According to Holleman (Rec. trav. chim. 1897, **16**, 162), dilituric acid and its homologues are aliphatic nitro-compounds in which the *iso-* form (*cf.* Hantzsch and Schultze, Ber. 1896, **29**, 699, 2251; Hantzsch and Veit, *ibid.* 1899, **32**, 607) is the stable modification. The aqueous solution of dilituric acid is faintly yellow and decomposes carbonates; the molecular conductivity for 1 g.-mol. dissolved in v litres of water is 323·4 (v=32), 341·4 (v=512), (μ_∞ should be 356); the acid is therefore almost completely dissociated in aqueous solution; the addition of one equivalent of a base does not appreciably change the colour of the solution, but on adding a second equivalent, the solution assumes the deep yellow colour characteristic of the aqueous solutions of the salts of this acid. Assuming that the formula



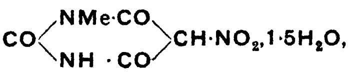
represents the constitution of the acid, Holleman states that the anion



is colourless and slowly hydrolyses into the yellow anion



Methyldilituric acid, 1-*methyl-5-nitrobarbituric acid,*



$$CO\left\langle\begin{matrix}NMe{\cdot}CO\\NH\ {\cdot}CO\end{matrix}\right\rangle CH{\cdot}NO_2,1{\cdot}5H_2O,$$

prepared by oxidising methylvioluric acid with concentrated nitric acid (Andreasch, Monatsh. 1900, **21**, 281), crystallises from aqueous solution, and the anhydrous acid is colourless; it melts and decomposes at 143°, is readily soluble in hot water, less so in cold water, alcohol, or acetone, and sparingly soluble in ether. The aqueous solution of the acid is intensely yellow and decomposes carbonates; the aqueous solutions of the salts are also yellow, but the solid salts are colourless or pale-yellow and sparingly soluble; the *potassium salt* $C_5H_4KO_5N_3$, the *sodium salt*

$$C_5H_4NaO_5N_3,H_2O,$$

the *ammonium salt* $C_5H_4(NH_4)O_5N_3$, are colourless; the *barium salt*,

$$(C_5H_4O_5N_3)_2Ba,H_2O,$$

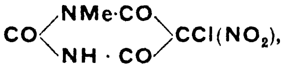
the *cadmium salt*,

$$(C_5H_4N_3O_5)_2Cd,2H_2O,$$

are pale-yellow; the *strontium salt*

$$(C_5H_4O_5N_3)_2Sr,3H_2O$$

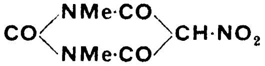
is colourless, but becomes yellow on losing its water of crystallisation. Methyldilituric acid is stable with bases; it reacts readily with chlorine to form 1-*methyl-5-chlordilituric acid*,



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{NH\cdot CO}\end{array}\right>\mathrm{CCl(NO_2)},$$

m.p. 121°; the corresponding bromo-compound melts and decomposes at 138°–139°.

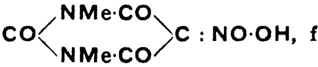
Dimethyldilituric acid, 1:3-*dimethyl-5-nitro-barbituric acid*,



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{array}\right>\mathrm{CH\cdot NO_2}$$

obtained by oxidising dimethylvioluric acid with concentrated nitric acid (Techow, Ber. 1894, **27**, 3085; Andreasch, Monatsh. 1895, **16**, 26); forms colourless microscopic crystals from acetone; dissolves in 5·98 parts of water at 14°, is sparingly soluble in alcohol, melts at 152° and changes into dimethylalloxan (Holleman, Rec. trav. chim. 1897, **16**, 162), and is reduced by hydriodic acid to dimethyluramil.

Dimethyldilituric acid is intensely yellow in aqueous solution, and this is due to the presence of the coloured anion of the *iso*nitro- form



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{array}\right>\mathrm{C : NO\cdot OH},$$

for on adding concentrated nitric acid, the colour almost entirely disappears; further, the molecular conductivity of the acid for 1 g.-mol. dissolved in v litres of water is 313·3 ($v=32$), and 337·6 ($v=1024$) (μ_∞ should be 352), so that in each solution the acid is almost completely ionised (Holleman, Rec. trav. chim. 1897, **16**, 162). The salts of dimethyldilituric acid are coloured, the *sodium salt* $C_6H_6NaO_5N_3\cdot H_2O$ is yellow, the *potassium salt* $C_6H_6KO_5N_3$ is greenish-yellow, the *magnesium salt* $(C_6H_6O_5N_3)_2Mg,4H_2O$ is yellowish-green, the *calcium salt*

$$(C_6H_6O_5N_3)_2Ca$$

is bluish-green, the *strontium salt*

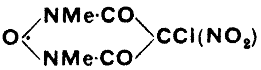
$$(C_6H_6O_5N_3)_2Sr$$

is pale-green, the *barium salt*

$$(C_6H_6O_5N_3)_2Ba,2H_2O$$

is rose-red, and the *silver salt* $C_6H_6AgO_5N_3$ is greyish-violet (Andreash, *l.c.*, and Monatsh. 1900, **21**, 295).

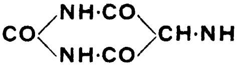
1 : 3-*Dimethyl-5-chlordilituric acid*,



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{array}\right>\mathrm{CCl(NO_2)}$$

prepared by passing chlorine into an aqueous solution of dimethyldilituric acid; melts and decomposes at 150°; the corresponding *bromo-derivative* melts partially at 152° (Andreasch, *l.c.*). Dimethyldilituric acid is readily decomposed by the action of bases forming water, carbon dioxide, and nitromalondimethylamide.

Amino derivatives of barbituric acids. *Uramil* (*murexan*), 5-*amino*-2:4:6-*trioxyhexahydropyrimidine*,



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{array}\right>\mathrm{CH\cdot NH_2},$$

was originally prepared by boiling alloxantin with ammonium chloride or ammonium thionurate with hydrochloric acid (Liebig and Wöhler, Annalen, 1838, **26**, 310); it is formed together with alloxan and ammonia when murexide is decomposed by acids (Beilstein, Annalen, 1858, **107**, 183), or by caustic alkalis (Reoch, Chem. News, 1875, **32**, 171); and is obtained when alloxanphenylhydrazone is reduced with tin and hydrochloric acid (Kühling, Ber. 1898, **31**, 1973). Uramil is conveniently prepared by reducing nitro- or nitrosobarbituric acid with hydriodic acid (Baeyer, Annalen, 1863, **127**, 223); or by heating ammonium dialurate, closed vessels being employed to avoid oxidation (Piloty and Finckh, *ibid.* 1900, **333**, 71). Uramil forms silky needles, insoluble in cold, sparingly soluble in hot water, it gives murexide on long boiling with ammonia; it has heat of combustion +380 kg.-cal., and heat of formation +170·7 kg.-cal. (Matignon, Ann. Chim. Phys. 1893, [vi], **28**, 289). Uramil forms metallic derivatives in which the iminohydrogen atoms are replaced by metals, *potassium uramil*

$$CO[NK\cdot CO]_2CH\cdot NH_2,2H_2O,$$

obtained in slender pale yellow needles by dissolving uramil in warm 50% potassium hydroxide solution, is converted by iodine into potassium murexide, and by methyl iodide into 1:3-dimethyluramil; the *acid potassium salt*

$$C_4H_5O_3N_3,C_4H_4O_3N_3K$$

forms colourless sparingly soluble leaflets; the *barium* and *lead* salts have also been prepared. 7-*Acetyluramil* forms crystalline salts, of which the *potassium, ammonium, silver, barium, lead,* and *copper* salts are described. 7-*Methyluramil* $CO[NH\cdot CO]CH\cdot NHMe$ is prepared from alloxantin and methylamine acetate; the *ethyl* derivative, $C_4H_4N_3O_3Et$, is similarly prepared (Piloty and Finckh, Annalen, 1904, **333**, 71; *cf.* Fischer, Ber. 1897, **30**, 561). 5-*Methyluramil*,

$$CO[NH\cdot CO]_2CMe\cdot NH_2,$$

m.p. 237° (corr.) is prepared by treating 5-bromo-5-methylbarbituric acid with alcoholic ammonia; 5-*ethyluramil* has m.p. 216° (corr.) (Fischer and Dilthey, Annalen, 1904, **335**, 334). 1-*Methyluramil* is prepared from methylalloxan and ammonium sulphite (Fischer, Ber. 1897, **30**, 3091). 1 : 3-*Dimethyluramil*,

$$CO[NMe{\cdot}CO]_2CH{\cdot}NH_2,$$

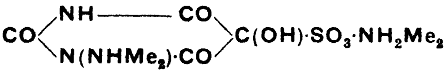
decomposes at 200° (Techow, *ibid.* 1894, **27**, 3087). 1 : 3 : 7-*Trimethyluramil* decomposes at 200° (Fischer, *ibid.* 1897, **30**, 559). 1 : 3-*Diethyluramil* decomposes at 200° (Sembritzki, *ibid.* 1897, **30**, 1814). 1 : 3-*Diphenyluramil*, m.p. 97°, forms a crystalline hydriodide readily soluble in cold water, with dissociation into hydrogen iodide and the uramil (Whiteley, J.C.S. 1907, **91**, 1340) ; *cp.* Fiore (Boll. Chim. farm. 1915, **54**, 449) for attempts to obtain 1-*amino* derivatives of alkylbarbituric acids.

Thionuric acid. *Sulpho-aminobarbituric acid* $CO[NH{\cdot}CO]_2CH{\cdot}NH{\cdot}SO_3H,1\frac{1}{2}H_2O$ is prepared by heating alloxan or violuric acid with a solution of ammonium sulphite (Liebig and Wöhler, Annalen, 1838, **26**, 268 ; Baeyer, *ibid.* 1863, **127**, 210). The free acid, obtained by decomposing the lead salt with sulphuretted hydrogen, is a crystalline mass, readily soluble in water, forming a strongly acid solution ; it is a dibasic acid yielding acid and normal salts, and is hydrolysed on boiling with water, yielding uramil and sulphuric acid. 1 : 3-*Dimethylthionuric acid* is obtained as its ammonium salt,

$$CO[NMe{\cdot}CO]_2CH{\cdot}NH{\cdot}SO_3NH_4,2H_2O,$$

by heating at 100° a solution of 1 : 3-dimethylalloxan with ammonium sulphite and ammonium bicarbonate (Techow, Ber. 1894, **27**, 3086), the salt loses $2H_2O$ at 105°, and decomposes at 180° ; the *barium salt* $C_6H_7N_3O_6SBa$, is also described.

Alloxandimethylamine sulphite



is obtained when alloxan is treated in aqueous solution with a neutral solution of dimethylamine sulphite, it is decomposed by dilute acids yielding sulphur dioxide, alloxantin, and dimethylamine, but no trace of substituted uramil (Piloty and Finckh, Annalen, 1904, **333**, 97).

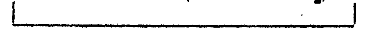
ψ-Uric acid, *carbamidobarbituric acid*,

$$CO[NH{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

prepared by boiling aminobarbituric acid with potassium cyanate (Baeyer, *ibid.* 1863, **127**, 3), or heating it with carbamide at 180° (Grimaux, Bull. Soc. chim. 1879 [ii], **31**, 535), forms prisms, sparingly soluble in cold water, and is converted by fusing with anhydrous oxalic acid, or by boiling with 25% hydrochloric acid, into uric acid. Pseudouric acid is a monobasic acid, and the *ammonium* $C_5H_5N_4O_4NH_4,H_2O$; *potassium* $C_5H_5N_4O_4K,H_2O$; *sodium*

$$C_5H_5N_4O_4Na,2H_2O,$$

barium $(C_5H_5N_4O_4)_2Ba,5H_2O$; *calcium* ; *lead* $(C_5H_5N_4O_4)_2Pb,2H_2O$; *copper* and *mercury* salts are crystalline. Biltz and Loewe, (Ber. 1934, **67** [B], 1199) suggest that the acidity is due to enolisation to the form



$$NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C(NH{\cdot}CO{\cdot}NH_2):C{\cdot}OH$$

7-*Methylpseudouric acid*,

$$CO[NH{\cdot}CO]_2CH{\cdot}NMe{\cdot}CO{\cdot}NH_2,$$

is prepared from 7-methyluramil and potassium cyanate (Fischer, Ber. 1897, **30**, 562). 1 : 3-*Dimethylpseudouric acid*,

$$CO[NMe{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

has m.p. 210° (Techow, *ibid.* 1894, **27**, 3088). 1 : 3 : 7-*Trimethylpseudouric acid* decomposes between 180° and 190° when slowly, and at 195° when rapidly heated (Fischer, *l.c.*). 1 : 3-*Diethylpseudouric acid* has m.p. 196° (corr.) with decomposition (Sembritzki, *ibid.* 1897, **30**, 1823). 1 : 3-*Diphenylpseudouric acid* melts and decomposes at 217° (Whiteley, J.C.S. 1907, **91**, 1341). 4-*Amino-ψ-uric acid* crystallises from hot water with $1H_2O$ in oblong plates (Levene and Senior, J. Biol. Chem. 1916, **25**, 607). The following pseudouric acids have also been prepared from the corresponding uramils : 9-allyl ; 7-methyl-9-phenyl ; 1 : 3-dimethyl-9-phenyl (Moore and Gatewood, J. Amer. Chem. Soc. 1923, **45**, 135) ; 1 : 7-dimethyl-9-phenyl (Gatewood, *ibid.*, p. 3056). Pseudouric acid is not alkylated by diazomethane in ether, methyl alcohol and hydrogen chloride, diethyl sulphate, or chloroformic ester (Biltz and Lemberg, J. pr. Chem. 1928 [ii], **118**, 222).

2-*Thio-ψ-uric acid*, colourless crystalline powder when hydrated, turns purple when dehydrated, decomposes above 300° (Johnson and Nicolet, J. Amer. Chem. Soc. 1914, **36**, 345).

9-*Allyl*-8-*thiopseudouric acid* has been prepared by treating uramil with aqueous potassium hydroxide and allyl *iso*thiocyanate (Biltz and Sauer, Ber. 1931, **64** [B], 752).

5-*Methoxy-ψ-uric acid*, m.p. 202°–204° (decomp.) ; 5-*chloro-ψ-uric acid*, m.p. 125° (decomp.) ; 5-*ethoxy-ψ-uric acid*, m.p. 227°–228° (decomp.) ; 5-*hydroxy-ψ-uric acid*, m.p. 210° (decomp.), reacts with bases to give the corresponding 5-*amino-ψ-uric acid*, of which the following have been prepared : *amino-*, m.p. 145°–147° (decomp.), *methylamino-*, m.p. 191°–192° (decomp.), *ethylamino-*, m.p. 170°–171° *dimethylamino-*, m.p. 191°–192° (decomp.), *diethylamino-*, m.p. 163°–165° (decomp.), and *anilino-*, m.p. 194°–196° (decomp.), and these on reduction yield the corresponding 7-*alkyl-* or 7 : 7 *dialkyl-uramils* (Biltz and Heyn, Annalen, 1916, **413**, 7).

Condensation of barbituric acids with aldehydes and ketones.—Barbituric acid and its 1- and 1 : 3-substituted derivatives condense readily, in the absence of condensing agents, with aldehydes or with dichloroketones to form alkylidene or arylidene derivatives of the types

$$CO[NH{\cdot}CO]_2C{:}CHR$$

and

$$CO[NH{\cdot}CO]_2C{:}CRR',$$

which on reduction yield the corresponding 5-alkyl (or aryl) barbituric acids

$$CO[NH{\cdot}CO]_2CH{\cdot}CH_2R$$

and $CO[NH{\cdot}CO]_2CH{\cdot}CHRR'$

These compounds are usually sparingly soluble, and barbituric acid and thiobarbituric acid can be used as quantitative precipitants for furfuraldehyde (Dox and Plaisance, J. Amer. Chem. Soc. 1916, **38**, 2156). 5-*Benzylidenebarbituric acid*,

$$CO[NH{\cdot}CO]_2C{:}CHPh,$$

m.p. 256°; and o-*nitrobenzylidenebarbituric acid*, m.p. 250°–252°, are colourless; *cinnamylidenebarbituric acid*, m.p. 226°–228°, and *furfurylidenebarbituric acid*, m.p. above 280°, are yellow (Conrad and Reinbach, Ber. 1901, **34**, 1339); p-*hydroxybenzylidenebarbituric acid*, m.p. 300°, is canary-yellow, and p-*dimethylaminobenzylidenebarbituric acid*, m.p. 282°, is orange-red (Weinschenk, *ibid.* 1685).

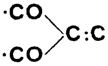
For the condensation products of thiobarbiacid with aromatic aldehydes, *see* Dox and Plaisance (*l.c.*); and for the use of thiobarbituric acid as a qualitative test for ketohexose, *see* Plaisance (J. Biol. Chem. 1917, **29**, 207).

1 : 3-*Diphenyl-5-benzylidenebarbituric acid*, $CO[NPh{\cdot}CO]_2C : CHPh$, exists in two forms, the stable form being yellow, and the labile form being colourless, each melts at 214°; 1 : 3-*diphenyl-5-cinnamylidenebarbituric acid*,

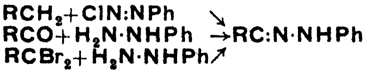
$$CO[NPh{\cdot}CO]_2C{:}CH{\cdot}CH{:}CHPh,$$

m.p. 268°, is orange-yellow; 1 : 3-*diphenyl-5-diphenylmethylenebarbituric acid*,

$$CO[NPh{\cdot}CO]_2{:}CPh_2,$$

m.p. 264°, is deep yellow. Each of the compounds described above contains the complex  consisting of three chromophores, yet each is coloured or colourless according to the nature of the radicles R and R′. It would seem that when R is hydrogen and R′ phenyl or its ortho- substituted derivative the compound is usually colourless, but that it is yellow when R′ is a para- substituted derivative of phenyl, or a more highly unsaturated radicle such as that afforded by cinnamaldehyde or furfuraldehyde; when both R and R′ are phenyl groups the compound is also yellow (Whiteley, J.C.S. 1907, **91**, 1332). These reactions have been further examined by Akabori (Proc. Imp. Acad. (Japan), 1927, **3**, 342; J. Chem. Soc. Japan, 1931, **52**, 601; Ber. 1933, **66** [B], 139) and Pavolini (Amer. Chem. Abstr. 1930, **24**, 3456) and numerous substances are described.

Condensation of barbituric acids with aromatic diazonium chlorides, and other reagents.—Barbituric acid and its 1 : 3-substituted derivatives condense readily with aromatic diazonium salts to form the aryl hydrazone of the corresponding alloxan, the same compound being obtained by the condensation of the arylhydrazine with the corresponding alloxan, or the 5 : 5-dibromo derivative of the barbituric acid



$$\begin{array}{l} RCH_2+ClN{:}NPh \searrow \\ RCO+H_2N{\cdot}NHPh \rightarrow RC{:}N{\cdot}NHPh \\ RCBr_2+H_2N{\cdot}NHPh \nearrow \end{array}$$

(R is $CO[NH{\cdot}CO]_2$)

(*v.* ALLOXAN).

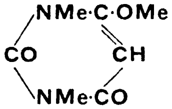
When 5-substituted derivatives of barbituric acid condense with aromatic diazonium salts the products are azo compounds of the type $CO[NR{\cdot}CO]_2CR'N{:}NR''$, these are readily hydrolysed by mineral acids yielding nitrogen, and the phenol corresponding with the aromatic diazonium salt, and regenerating the barbituric acid,

$$CO[NR{\cdot}CO]_2CR'N{:}NR'' \rightarrow CO[NR{\cdot}CO]_2CHR'+N_2+R''OH$$

5-*Benzeneazo*-1 : 3-*diphenyl*-5-*benzylbarbituric acid*, $CO[NPh{\cdot}CO]_2C(CH_2Ph){\cdot}N{:}NPh$, m.p. 170°–171°, forms bright yellow prisms; the p-*nitro* derivative crystallises in bright yellow prisms, m.p. 181°–182°; 5-*benzeneazo*-1 : 3-*diphenyl-5-diphenylmethylbarbituric acid*,

$$CO[NPh{\cdot}CO]_2C(CHPh_2){\cdot}N{:}NPh$$

bright yellow prisms, m.p. 160°; the p-*nitro* derivative forms canary-yellow prisms, m.p. 175° (Whiteley, J.C.S. 1907, **91**, 1344). Barbituric acid reacts with diazomethane to yield a *trimethylbarbituric acid*,

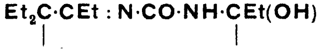


m.p. 164°–166° (Herzig, Z. physiol. Chem. 1921, **117**, 13), and with carbamazide, hydrated barbituric acid gives *malobiuric acid*,

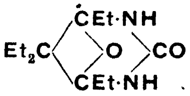
$$CO{\cdot}[NH{\cdot}CO]_2{\cdot}CH{\cdot}CO{\cdot}NH_2$$

(Curtius, Ber. 1923, **56** [B], 1577).

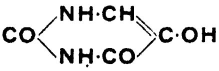
Dox (J. Amer. Chem. Soc. 1927, **49**, 2275) has shown that diethylbarbituric acid reacts with ethylmagnesium bromide to yield a compound, $C_{12}H_{22}O_2N_2$, which may be either



or



isoBarbituric acid, 5-*hydroxyuracil*



is one of the products obtained by the reduction of nitrouracil; it forms an *acetyl* derivative, and when treated with bromine water yields *iso*dialuric acid (*q.v.*) (Behrend and Roosen, Ber. 1888, **21**, 999). Oxidised with alkaline potassium ferricyanide, it yields 4 : 4′-di-*iso*-barbituric acid (Davidson and Baudisch, J. Biol. Chem. 1925, **64**, 619).

M. A. W.

BARILLA or BARILLOR. (Fr. *Barille.*) Commercial name of an impure soda obtained from the ashes of the *Salsola soda* (Linn.), formerly grown specially in Spain, Sicily, Sardinia, the Canary Islands and the Levant. The ash which contains about 20% alkali, together with the chlorides and sulphates of sodium, calcium and aluminium, was used for making soda-soap.

BARIUM. Symbol, **Ba.** At. wt. 137·36.

The name " barote " (from βαρύς, heavy) was given to the earth contained in heavy-spar (*terra ponderosa*) by Guyton de Morveau in 1779, and was afterwards altered to " baryta " by Lavoisier ; the name itself, therefore, is indicative of the great density of its compounds.

The metal is not found native ; its oxide, baryta, **BaO**, was first recognised as a peculiar earth distinct from lime by Scheele in 1774.

Most igneous rocks contain small but variable amounts of barium oxide. Holmes and Harwood (Quart. J. Geol. Soc. 1932, **351**, 423) give a table of collected analyses from which the following examples are taken and indicate that **BaO** and **SrO** are mostly associated with rocks rich in potash and lime.

No. of analyses.	Rock family.	Average percentage.	
		BaO	SrO
28	*Leucitite*	0·43	0·18
16	*Leucite-tephrite*	0·25	0·12
10	*Minette*	0·24	0·07
75	*Syenite*	0·17	0·06
14	*Tephrite*	0·17	0·09
13	*Nephelinite*	0·13	0·05
34	*Phonolite*	0·13	0·05
222	*Gabbro*	0·05	0·01
116	*Granite*	0·04	0·01

Limestones show from 0·001 up to 0·5% of $BaSO_4$ and more. Sea-water contains traces of barium and strontium, as do also many natural brines. *Barytes* is a common gangue mineral in many ore deposits where it is scarcely of economic importance.

Barium occurs principally in nature as the sulphate, *baryte* or heavy-spar $BaSO_4$, and is found frequently in association with metallic sulphide ores such as *galena* ; less abundantly as *witherite* $BaCO_3$, *barytocelestite*

$$(BaSrCa)SO_4,$$

barytocalcite ($BaCO_3{\cdot}CaCO_3$), *alstonite* $(BaCa)CO_3$; in small quantities in most ores of manganese ; in certain silicates, such as *brewsterite* $H_4(SrBa)Al_2Si_6O_{18},3H_2O$, *harmotome* $H_2(K_2Ba)Al_2Si_5O_{15},4H_2O$, and *hyalophane* or baryta-felspar $K_2Ba,2Al_2Si_8O_{24}$; and frequently in mineral waters. Barium is also found in calcium and strontium minerals, replacing a portion of these elements with which it is isomorphous.

Preparation.—Davy (Phil. Trans. 1808, 354) electrolysed a moist paste of a barium salt, using a cathode of mercury. He thereby obtained a poor amalgam which on distillation yielded a silver-white solid that he believed to be metallic barium, but which, as shown by Donath, was only a rich amalgam (Ber. 1879, **12**, 745).

Guntz prepared a 3% amalgam by Davy's method which was then distilled under reduced pressure in hydrogen to obtain a 10% amalgam of close grain. This, on further heating, liquified at 900° giving an amalgam which on solidification had a coarsely faceted crystalline structure and contained 65% **Ba.** By further heating to 950° barium was obtained containing **Ba** 98·35, **Hg** 0·83, **Fe** 0·40 (Compt. rend. 1905, **141**, 1240). Later he modified the process by first converting the metal into hydride at 900° in a current of hydrogen and then decomposing the hydride by heating to 1,200°. By this means he obtained a metal containing 99·5% **Ba.**

The second method which has been much used, also due to Guntz (Compt. rend. 1906, **143**, 339), is to heat the oxide with one-tenth its weight of aluminium at 1,200°. The metal condenses in the cooler part of the tube and assays as much as 98·8% **Ba.** Danner somewhat modified the process as follows and claims to have obtained very pure **Ba** (J. Amer. Chem. Soc. 1924, **46**, 2382). The pure oxide was partly converted to peroxide (10%), which was then reduced by mixing with coarse aluminium and striking an arc to the mass. The cold fused mass was ground and the fine particles sifted off ; the remaining metal was sealed in a distillation apparatus which was evacuated as soon as possible. When the pressure reached 10^{-4} mm. the temperature was raised to 950° and the metallic barium distilled off to form crystalline pellets.

Matignon (Compt. rend. 1913, **156**, 1378) obtained barium by heating the oxide (3 mols.) with silicon (1 atom) in an evacuated steel tube, at 1,200°. The metal distils off and condenses in the cooler part of the tube, the reaction being :

$$3BaO+Si=BaSiO_3+2Ba-37 \text{ cals.}$$

The silicon can be replaced by ferro-silicon containing 95% silicon.

The preparation of the metal by electrolysis of the fused oxide or chloride does not appear to be attended with success ; sub-salts are formed, and the current passes without further action (Z. Elektrochem. 1903, **9**, 291).

Matthiessen (Annalen, 1855, **93**, 277) electrolysed the fused chloride and obtained metallic-looking globules which were probably subchloride. B. Neumann and E. Bergve (Z. Elektrochem. 1914, **20**, 187), however, state that **Ba** like **Sr** and **Ca** can be obtained in sticks 10 cm. long and 1 to 2 cm. diameter by electrolysis of a fused mixture of **Ba** and **K** chloride.

Guntz (Chim. et Ind. 1929, **21**, Nr. 2, 458) states that previously pure barium had not been prepared. A high percentage product with only 98·35 barium is obtained when barium amalgam is heated for a long time in a vacuum container. By electrolysis of $BaCl_2$ a subchloride **BaCl** is obtained. Preparation of pure barium hydride by heating barium amalgam in a stream of hydrogen, and decomposition of this compound *in vacuo*, gives crystals of pure barium. Reduction of the oxide with magnesium gives no metal but a suboxide.

Properties.—Barium when pure is a silver-white metal with a density of 3·78, slightly harder than lead, melts at about 850° and commences to volatilise at 950°. Barium oxidises rapidly in air, yielding principally the monoxide ; the powder easily takes fire spontaneously. Guntz states that molten barium attacked nearly all the metals, iron and nickel being the most resistant. Barium decomposes water and alcohol in the cold yielding, in the latter case, barium ethoxide. Carbon dioxide has no action on it. With hydrogen it forms the hydride BaH_2 and with nitrogen the nitride Ba_3N_2. It unites with ammonia giving barium ammonia $Ba(NH_3)_6$.

The melting-point of barium containing 1·7% Fe and 0·8% N is 658°±1° (Hartmann and May, Z. anorg. Chem. 1929, **185**, 167).

Barium crystallises in the cubic system, but the lattice is space-centred with a=5·01Å ; atom radius 2·17Å (Ebert and Hartmann, Z. anorg. Chem. 1929, **179**, 418).

Barium amalgam.—In addition to the method employed by Davy and Guntz, given above, barium amalgam was prepared by Crooks (Chem. News, 1862, **6**, 199) by digesting a saturated solution of $BaCl_2$ with Na amalgam. P. P. Fedotéev and I. Weizer (Z. anorg. Chem. 1914, **86**, 325) investigated the various factors for obtaining maximum values. The electrolysis of liquid amalgam by Kremann, Bauer, Vogrin and Scheibel (Monatsh. 1930, **56**, 35) showed that Ba migrates to the anode up to 2·7% concentration beyond which a reversal in migration occurs towards the cathode.

Barium alloys.—Lead alloys are obtained by the use of fused $BaCl_2$ 8 parts, KCl 5 parts, and NaCl 3 parts in a cell with carbon anode and molten lead as cathode. An alloy containing 10% barium requires a temperature of 650° using 4–6 volts with electrodes 1–1·5 cm. apart and a current density not exceeding 3 amp./cm.^{2} at the anode and 1 amp./cm.^{2} at the cathode. Alloys of lead have been prepared with 18% barium and less than 1% sodium. Similarly alloys with tin and zinc can be prepared.

Thermal analysis of silver-barium (up to 60% Ba) shows the occurrence of the following compounds: Ag_4Ba, m.p. 729°, d^{25}_{4} 7·93; Ag_5Ba_3, d^{25}_{4} 6·70 ; Ag_3Ba_2, m.p. 848°, d^{25}_{4} 6·60 (Weibke, Z. anorg. Chem. 1930, **193**, 297).

Ray and Thompson (Metals and Alloys, 1930, **1**, 314) prepared alloys of tin and barium by the electrolysis of a eutectic mixture of potassium and barium chlorides over a molten tin cathode in a chromium-plated iron crucible, a carbon rod being used as anode. The compounds $BaSn_3$ and $BaSn_5$ are present in alloys containing up to 28% barium. $BaSn_3$ is stable and $BaSn_5$ unstable above 422°. The alloys corrode rapidly in air to form a film of oxide and carbonate which inhibits further action ; with water hydrogen is evolved. Addition of barium increases the hardness and brittleness of the alloy.

Oxides of barium.—Three oxides of barium are known—barium suboxide Ba_2O, barium oxide or baryta BaO, and barium peroxide BaO_2.

Barium suboxide Ba_2O is obtained, according to Guntz (Compt. rend. 1906, **143**, 339), by heating the protoxide with magnesium or barium to a temperature of 1,100°. It is a black mass which decomposes water.

Barium oxide, protoxide, monoxide, or baryta, BaO, is the oxide formed when the metal burns in air. It is more readily obtained by heating (1) the nitrate or (2) the carbonate of barium.

(1) Barium nitrate heated progressively, fuses, then decomposes with the liberation of nitrous fumes and much frothing leaving a porous mass of barium oxide.

(2) The carbonate may also be converted into barium oxide by exposing it to the strongest heat of a forge fire ; but the last traces of carbon dioxide are only expelled with difficulty. However, at an ordinary white heat, this may be accomplished by mixing the carbonate with one-tenth of its weight of lampblack or charcoal and making into a thick paste with oil or tar, carbonic oxide being evolved, thus:

$$BaCO_3+C=BaO+2CO.$$

The mixture should be heated in an earthen crucible lined with lampblack and fitted with a tight cover ; on the large scale witherite is thus converted into baryta for use in separating crystallised sugar from molasses. In a second baryta-manufacturing process a mixture of the carbonates of barium and calcium is ignited in a current of aqueous vapour.

(3) On the small scale, baryta may be easily obtained by heating barium iodate, which readily gives up all its iodine, together with five-sixths of its oxygen, without fusing or frothing :

$$Ba(IO_3)_2=BaO+I_2O_5.$$

Barium oxide as prepared by the above methods is generally a greyish-white friable mass of sp.gr. 4·7–5·5. Brügelmann (Wied. Ann. 1878, **4**, 277) by heating barium nitrate in a porcelain flask, obtained minute crystals of BaO, sp.gr. 5·722, belonging to the regular system. He found later that by heating the oxide in a clay or graphite crucible he obtained needles, sp.gr. 5·32, belonging to the hexagonal system, but if heated in a platinum crucible the oxide is obtained in cubic forms, sp.gr. 5·74. It is therefore dimorphous (Brügelmann, Z. anal. Chem. 1890, **29**, 127).

A loosely granular form of barium oxide with a purity of about 90% is produced by heating a mixture of the carbonate with 25–30% coke (preferably from petroleum) at 1,200°–1,300°. The excess of carbon serves to prevent the mass sintering and is removed by heating in a current of air or steam at about 1,300°. The variety so formed is particularly suitable for making barium peroxide for the manufacture of hydrogen peroxide (Askenasy and Rose, Z. anorg. Chem. 1930, **189**, 1).

P. Baud (Compt. rend. 1928, **186**, 438) states that a mixture of equal parts of Fe_2O_3 and Cr_2O_3 with 5 times $BaCO_3$ heated to 1,160° yields a 57–59% BaO product. If 100 parts $BaCO_3$ and 15 (about) Fe_2O_3 and a mixture of $CaCO_3,MgO,Cr_2O_3$ is heated to 1,150°, a 78% BaO product is obtained.

Barium oxide can be melted in the oxy-hydrogen blow-pipe flame ; but in the electric furnace it may be readily liquefied and volatilised. The liquid on cooling yields a crystalline mass (Moissan, Ann. Chim. Phys. 1895 [vii], **4**, 139) ; it is a non-conductor of electricity, but in presence of mercury may be electrolysed into barium and oxygen. BaO is strongly alkaline, caustic, and poisonous. It is deoxidised by potassium at a red heat. Fluorine attacks it in the cold, liberating oxygen, the mass becoming incandescent. Dry chlorine has little or no action on perfectly anhydrous baryta. It slakes with water, forming barium hydroxide $Ba(OH)_2$ with such energy that the whole mass becomes incandescent provided the amount of water be not too large. It rapidly absorbs moisture from the air. It unites with methyl and ethyl alcohols, forming the compounds $BaO,2CH_4O$ and $BaO,2C_2H_6O$. Heated in the vapour of carbon disulphide, it forms barium carbonate and barium sulphide:

$$3BaO+CS_2=BaCO_3+2BaS.$$

It dissolves readily in dilute nitric and hydrochloric acids, but with many other acids forms insoluble salts. When heated to low redness in a glass tube in the vapour of sulphuric anhydride, formation of barium sulphate $BaSO_4$ occurs with incandescence.

Booth and McIntyre (Ind. Eng. Chem. 1930, **2**, 12) recommend the use of anhydrous barium oxide as a desiccating agent, stating that the amount of water vapour left in a gas after passage through a tube containing the material is only 1 mg. in 10,000 litres. The porous oxide prepared by low temperature decomposition of barium carbonate is best, and on account of its expansion on hydration it should be used in conjunction with glass wool or other packing materials.

Barium peroxide, or dioxide, BaO_2, is formed when anhydrous baryta is heated to a dull red heat in a stream of oxygen or of air freed from carbonic acid. Barium hydroxide may be similarly converted into the peroxide, but less readily, as it fuses below the temperature of absorption of oxygen; the absorption, however, may be rendered rapid by mixing the hydroxide with lime or magnesia which prevents fusion and keeps the mass porous. Peroxide of barium may also be obtained by sprinkling red-hot baryta with four times its weight of powdered potassium chlorate in successive small portions; the potassium chloride simultaneously formed may be washed out with water, leaving the peroxide in the form of a hydrate.

The peroxide obtained by these means is not pure, being contaminated with a little unconverted barium oxide, iron, silica and other substances derived from the containing vessels. In order to purify it the finely powdered crude product is gradually added to an excess of dilute hydrochloric acid, avoiding any considerable rise of temperature; the crude substance dissolves, forming barium chloride and hydrogen peroxide. The solution is filtered from insoluble matters and treated with baryta water until the silica and ferric oxide, together with a little hydrated barium peroxide regenerated by action of the hydrogen peroxide upon the barium hydroxide, are precipitated. The liquid is again filtered and then supersaturated with baryta. By this means the whole of the hydrogen peroxide regenerates barium peroxide, which is precipitated in minute prisms or laminæ of the hydrate $BaO_2,8H_2O$, in which condition it is best preserved, and is a suitable form for use in the preparation of hydrogen peroxide. On drying at 130° or at ordinary temperatures *in vacuo* it is converted into anhydrous barium peroxide.

The preparation of barium peroxide in the wet way always yields the octohydrate when more than one molecule of baryta is present per molecule of H_2O_2. Above 60° it is formed, whatever the composition of the solution. Below 40° the di-peroxyhydrate $BaO_2,2H_2O_2$ is obtained from solutions containing much H_2O_2. A compound BaO_2,H_2O_2 may be obtained between 30° and 60° (Z. anorg. Chem. 1904, **89**, 405).

Barium peroxide is a grey, impalpable powder, slightly more fusible than the monoxide. The tension of dissociation varies with the temperature. According to Le Chatelier (Compt. rend. 1892, **115**, 654), the figures are as follows:

Temp. C.°	520	555	650	670	720	735	750	775	785	790
Press. mm.	20	25	65	80	210	260	340	510	620	670

These pressures vary according to the degree of decomposition being highest at the commencement of the operation. Brin's method of preparing oxygen depends upon the above physical factors. The spongy protoxide of barium prepared as indicated above is placed in thin beds in iron retorts heated by special furnaces. The temperature is maintained between 500° and 600° and air, which has been freed from moisture and carbon dioxide by passing first over quicklime and then over caustic soda, is forced by pumps through the retorts whereby the BaO is converted to BaO_2, the residual nitrogen being allowed to escape into the atmosphere. When the peroxidation is complete a set of valves places the retorts in connection with the exhaust pumps, the reduction of pressure causing liberation of oxygen. The first portions are allowed to escape until the pressure measures 65 cm. mercury, another set of valves then comes into play and automatically connects the retorts with the gasometer. The oxygen obtained is 97 to 98% pure. Barium peroxide is used in the preparation of hydrogen peroxide and as a bleaching agent in acid solution.

The decomposition of barium peroxide by heat at atmospheric pressure has been followed by means of a temperature curve. The reaction is endothermic. The temperature at which the vapour pressure of the cooled oxygen is equal to 760 mm. was found to be 795°, which agrees with the value 796° found by Le Chatelier. The higher temperature 825° obtained by Hildebrand is accounted for by the use of carefully dried materials, for, in the absence of moisture, the reaction is very slow and incomplete. In presence of CuO barium peroxide begins to decompose at 200°, and decomposition becomes vigorous at 625°–660° (Hedvall, Z. anorg. Chem. 1918, **104**, 163–168).

Barium peroxide is decomposed by hydrogen sulphide at ordinary temperatures, and when heated in a current of carbonic oxide it becomes white hot. It becomes incandescent when heated in sulphur dioxide. When treated with strong sulphuric acid at a temperature exceeding 70°, oxygen is given off ; at lower temperatures the oxygen is mixed with ozone. When the peroxide is mixed with dilute acid in presence of silver oxide, manganese dioxide or lead peroxide, oxygen is evolved both from the barium peroxide and from the other oxide. A small quantity of a silver compound is capable of decomposing a large quantity of barium peroxide, but iodine decomposes an exactly equivalent quantity :

$$BaO_2+I_2=BaI_2+O_2.$$

The amount of active oxygen in BaO_2 may be determined by adding a known quantity of the peroxide to pure hydrochloric acid, then potassium iodide free from iodate together with excess of bicarbonate of soda, and titrating the liberated iodine with a standard solution of sodium thiosulphate. It may also be estimated by titrating an acid solution with standard potassium permanganate (Bertrand, Bull. Soc. chim. 1877 [ii], **33**, 148).

Barium tetroxide.—The yellow colour formed when the substance BaO_2,H_2O_2 is kept at atmospheric temperature is probably due to the formation of the tetroxide BaO_4, which is highly unstable (Traube and Schulze, Ber. 1921, **54** [B], **35**, 1626).

Barium hydroxide, *hydrate of baryta*, or *caustic baryta*, $Ba(OH)_2$ or $BaO{\cdot}H_2O$, is formed, with great evolution of heat, when water is added to anhydrous baryta (barium oxide) :

$$BaO+H_2O=Ba(OH)_2.$$

A hot concentrated solution of equivalent quantities of barium nitrate and sodium or potassium hydroxide deposits, on cooling, crystals of barium hydroxide. Caustic soda is usually employed, of sp.gr. 1·10–1·15, and the crystals obtained are freed from mother liquor by draining, or better, by means of a centrifugal machine.

Commercial caustic baryta is prepared on the large scale by igniting the native sulphate or heavy spar with coal or charcoal, whereby an impure barium sulphide is obtained ; this is converted into carbonate by heating it in earthenware retorts in a current of moist carbon dioxide :

$$BaS+CO_2+H_2O=BaCO_3+H_2S.$$

Superheated steam is then passed over the heated carbonate, when the following decomposition takes place :

$$BaCO_3+H_2O=Ba(OH)_2+CO_2.$$

R. Heintz (Chem.-Ztg. 1901, **25**, 199) reviews the methods that have been suggested for the manufacture of baryta from baryte, and considers them too costly for the production of a cheap commercial oxide; only the carbonate is used to any extent. The calcination is conducted in specially constructed furnaces lined with basic material and heated with producer gas. The product contains 95% BaO.

Marino *et al.* (Gazzetta, 1913, **43**, i, 416, 423, 434 ; ii, 1) have shown that the reduction of barium sulphate to sulphide is effected by reducing gases, especially water gas, more readily than with the use of coal, the reduction occurring at 525°–540°. In practice the temperature is 600°–625°, and a yield of 95–98% was obtained in an experimental furnace. Baryta is then prepared by the electrolysis of a solution of barium sulphide by Brochet and Ranson's process (Compt. rend. 1903, **136**, 1195) a diaphragm of high resistance being employed in all cases. The best results are obtained with copper electrodes and a solution containing 20% of BaS. The barium hydrate at the anode increases as long as the concentration does not fall below 5%, and in concentrated solutions, at 70°–80° amounts, after 24 hours, to 13 g. per litre. Formation is due to interaction of hydroxyl ions with the BaS.

Terres and Brückner (Z. Elektrochem. 1920, **26**, 1–24) show that $Ba(OH)_2$ and $Ba(SH)_2$ cannot exist together in the same solution, but form a compound

$$OH{\cdot}Ba{\cdot}SH,5H_2O$$

consequently, pure $Ba(OH)_2$ cannot be crystallised from a solution obtained by the action of water on barium sulphide.

A new method of preparing barium hydroxide is as follows (F.P. 633368 of 26/4/27). Commercial barium sulphate is heated with silica to at least 1,500°, and the resulting polybasic silicate $(BaO)n,SiO_2$ broken up and extracted with water to separate the barium hydroxide solution from insoluble silicate, etc. The waste gases are used to manufacture sulphuric acid. Deguide uses 1 mol. SiO_2 to 4 mols. $BaCO_3$, and a temperature of 1,300° (Moniteur Produits Chem. 11, **106**, 6–8 ; Swiss P. 122352, 8/10/26).

Barium hydroxide crystallises from water in large, transparent, colourless, quadratic prisms capped by pyramids. The crystalline form is stated by Natta to be rhombohedral. The crystals $Ba(OH)_2,8H_2O$ are isomorphous with the corresponding strontium compound. They dissolve in 20 parts of water at 15°, and in 2 parts of boiling water. The aqueous solution known as baryta water is highly caustic and of strong alkaline reaction, rapidly becoming covered with a film of carbonate owing to absorption of atmospheric carbon dioxide ; hence it is frequently used in the determination of the amount of carbon dioxide contained in the air. On exposure to air the crystals fall to a white powder, with loss of seven molecules of water. de Forcrand (Compt. rend. 1886, **103**, 59) isolated the hydrate $Ba(OH)_2,H_2O$ by allowing the compound $BaO,2MeOH+2H_2O$ to stand over sulphuric acid *in vacuo*. H. Lescœur (Compt. rend. 1883, **96**, 1578) showed that at 100° $Ba(OH)_2,H_2O$ has a tension of dissociation of 45 mm., and that this hydrate is completely converted to $Ba(OH)_2$ when heated to 100° *in vacuo*. Lescœur also proves that the dissociation tension of $Ba(OH)_2,8H_2O$ is 213 mm. at 75°, so that at this temperature all three hydrates of BaO may exist simultaneously. $Ba(OH)_2$, when heated alone, is only reduced to baryta above a red heat ; if not heated above redness it re-forms, on cooling, a crystalline mass of $Ba(OH)_2$, but when heated in a current of air it takes up oxygen and is converted into barium peroxide with loss of water ; when heated in a current of carbon dioxide it also loses water and is converted into barium carbonate :

$$Ba(OH)_2+O=BaO_2+H_2O$$

$$Ba(OH)_2+CO_2=BaCO_3+H_2O$$

Baryta has been used in the processes of sugar-refining, inasmuch as it forms with cane-sugar the compound $C_{12}H_{22}O_{11},BaO$, which, when treated with carbon dioxide, is decomposed into sugar and insoluble barium carbonate, hence affording a means of separating the pure sugar from the molasses; but the baryta is now replaced by the non-poisonous strontium hydroxide in this process.

Hydrated barium peroxide.—Schöne has shown (Ber. 1880, **13**, 803) that only one hydrate of BaO_2 exists, containing 8 mols. of water, $BaO_2,8H_2O$. This hydrate is precipitated in crystalline scales when hydrogen peroxide is added to concentrated solutions of barium hydroxide. It is slightly soluble in cold water, but decomposes in boiling water, forming $Ba(OH)_2$ and evolving oxygen.

Barium subchloride was stated to be obtained by Guntz (Bull. Soc. chim. 1903 [iii], **29**, 490) when equal amounts of $BaCl_2$ and Ba were heated together *in vacuo* at 850°. The fragments of $BaCl_2$ absorbed the molten barium without change, yielding a microcrystalline product. The material so obtained was not pure and decomposed water. By using Na, a product, NaCl·BaCl, can be obtained. BaCl appears to be formed when electrolysing fused $BaCl_2$. Marino (Atti R. Accad. Lincei, 1915 [v], **24**, ii, 143) is of opinion that the supposed barium subchloride and the compound BaCl·NaCl are solid solutions of barium and sodium respectively in ordinary barium chloride.

Barium chloride, $BaCl_2$. Crystallised (*terra ponderosa salita*) $BaCl_2,2H_2O$. Barium chloride may be prepared either from witherite, the native carbonate, or from heavy-spar, the native sulphate. The witherite is dissolved in dilute hydrochloric acid and the solution allowed to stand some time in contact with excess of the carbonate, which is added to precipitate iron and other foreign metals present in the mineral; the rapidity of precipitation is much increased by the addition of a little baryta water. The filtered liquid is then neutralised with hydrochloric acid, and the salt crystallised out and purified by recrystallisation.

From the native sulphate barium chloride may be prepared in two ways:

(1) By heating the sulphate in a crucible with powdered coal and decomposing with hydrochloric acid a filtered solution in water of the barium sulphide thus formed

$$BaS+2HCl=BaCl_2+H_2S$$

Excess of hydrochloric acid is added, and the liquid boiled till free from sulphuretted hydrogen; it is then filtered, cooled and evaporated to the crystallising point.

(2) By heating a mixture of 100 parts finely powdered heavy-spar, 40 parts of charcoal, 20 parts of limestone, and 50 parts of calcium chloride to a red heat in a reverberatory furnace, by which barium chloride and calcium sulphide are formed. The mass is lixiviated with water, when the barium chloride is dissolved out, leaving an insoluble calcium oxysulphide formed by the union of the sulphide with the oxide of calcium produced by ignition of the limestone.

Commercial barium chloride generally contains small quantities of strontium and calcium chlorides, together with traces of the chlorides of iron, aluminium, copper and lead. Washing the crystals with alcohol removes both the strontium and calcium chlorides, whilst calcium chloride may also be removed by digesting with barium carbonate suspended in water, when the calcium chloride becomes converted to carbonate or, more rapidly, by adding baryta water and passing carbon dioxide into the liquid. Digestion with barium carbonate also precipitates the sesquioxides of iron and alumina. Lead and copper may best be removed by the addition of a little barium sulphide.

Barium chloride may be recovered from mixtures of chlorides of the alkalis and alkaline earths by treating the concentrated liquor with a hot saturated solution of salt, when on cooling a mixture of barium and sodium chlorides crystallises out; by treating a cold saturated solution of this mixture with twice its volume of hydrochloric acid, barium chloride is precipitated (Dingl. polyt. J. 1884, **250**, 91).

Barium chloride crystallises from aqueous solution with two molecules of water as $BaCl_2,2H_2O$ in transparent, colourless, rhombic tables; sp.gr. 2·66–3·05. The crystals decrepitate when heated. They have an unpleasant, bitter, sharply saline taste, exciting nausea and are very poisonous.

A monohydrate is prepared by shaking $BaCl_2,2H_2O$ (dihydrate) with 99% methyl alcohol and filtering rapidly to remove the small amount of undissolved salt. After a few minutes the monohydrate separates from the solution in colourless rhombic plates. It can be dried over $CaCl_2$ in a vacuum. At 14°, 100 c.c. of methyl alcohol dissolves about 2·5 g. of monohydrate (Kirshner, Z. physikal. Chem. 1911, **76**, 174).

One hundred parts of water at 0° dissolve 32·62 parts of anhydrous barium chloride, and 0·2711 part for every degree above 0°; 100 parts of water at 15·6° dissolves 43·5, and at 105·5° 78 parts of the crystallised chloride. One part of crystallised barium chloride at 18·1° dissolves in 2·257 parts of water to form a solution of sp.gr. 1·28251 (Karsten). A solution saturated at 8° has a sp.gr. of 1·270 (Anthon).

Barium chloride is almost insoluble in strong hydrochloric acid, so that it is precipitated from its solutions by hydrochloric acid, and a few drops of the acid reduce the solubility considerably. Hot absolute alcohol dissolves only $\frac{1}{400}$ part of the crystals; but according to Fresenius, 1 part of the salt dissolves in 8,108 parts of alcohol of 99·3% at 14°, and in 4,857 parts of the same alcohol at its boiling-point.

The heat of solution of anhydrous barium chloride in aqueous solutions of alcohol containing 20·36 and 33·83 alcohol are −130 and −944 g.-cal. respectively; the corresponding values for the hydrated salt $BaCl_2,2H_2O$ are −6,718 and −7,416 g.-cal. The heats of hydration are thus +6,588 and +6,472 g.-cal. in the two cases, indicating that the addition of alcohol to water lowers the heat of hydration which in the case of pure water is 7,465 (De Kolosovski, J. Chim. phys. 1925, **22**, 97).

The crystals of $BaCl_2,2H_2O$ are not efflorescent, but give up the whole of their water at 100°, leaving a white mass of the anhydrous salt, which melts at a red heat, forming a translucent mass on cooling ; the crystals are monoclinic, of prismatic habit, $a:b:c=0{\cdot}6177:1:0{\cdot}6549$ $\beta=91°\ 5'$ (Wyrouboff, Bull. Soc. franç. Min. 1886, **9**, 262), optically biaxial and positive. The specific gravity of the anhydrous chloride is given by various observers as 3·70 to 4·15. Hans Winter (Diss. Leipzig, 1913, 1–46) gives the following constants, m.p. 958°, sp.gr. 3·789. When heated in a current of steam below its fusing-point it evolves hydrochloric acid.

Calcium and barium chlorides form the double salt $CaCl_2,BaCl_2$ (m.p. 631°), but no mixed crystals. Barium and strontium chlorides form a complete series of regular (β) mixed crystals, which on cooling are transformed to (α) crystals (monoclinic). The two series correspond with the α and β forms of $BaCl_2$, which co-exist in equilibrium at 922°. The freezing-point curve shows a minimum at 847°, at which point 30 mols. % $BaCl_2$ are present. The double chlorides $2KCl,SrCl_2$ and $2KCl,BaCl_2$ are isomorphous and rhombic.

Hans Winter shows that $BaCl_2$, m.p. 958°, *d* 3·789, is optically biaxial and positive while barium fluoride, m.p. 1,289°, $SrCl_2$, m.p. 874°, *d* 3·054, and SrF_2, m.p. 0·1400° are all cubic in crystallisation. These do not form mixed crystals but the double salts $BaCl_2,BaF_2$, m.p. 1,008°, *d* 5·931, $SrCl_2,SrF_2$, m.p. 962°, *d* 4·616, are each tetragonal and optically negative.

A concentrated solution of barium chloride is decomposed by sodium or potassium nitrate, forming barium nitrate and a chloride of the alkali-metal. With glycocol, $CH_2(NH_2){\cdot}COOH$, it forms a crystalline compound. It acts upon blood, preventing putrefaction and coagulation.

Barium chloride is extensively used as a reagent, especially for the detection and estimation of sulphuric acid. It is also used for the preparation of artificial barium sulphate or " permanent white."

Barium oxychloride.—André (Compt. rend. 1881, **93**, 58) obtained an oxychloride of barium by adding 60 g. of $Ba(OH)_2$ to 200 g. of crystallised barium chloride, and boiling the mixture with 500 g. of water, filtering, and allowing to cool, when nacreous lamellæ separated, to which he ascribed the formula $BaCl_2{\cdot}BaO,5H_2O$ (Compt. rend. 1884, **98**, 572). Beckmann (J. pr. Chem. 1883 [ii], **27**, 126) also obtained nacreous plates by similar means to which he gave the formula $BaCl(OH),2H_2O$. These plates lose four-fifths of their water at 120° and the remaining fifth at the fusing-point by prolonged heating in a stream of hydrogen. This oxychloride is readily decomposed by water or alcohol.

Barium chlorite, $Ba(ClO_2)_2$, may be obtained free from chloride by the action of a mixture of carbon dioxide and chlorine dioxide free from chlorine on barium peroxide suspended in hydrogen peroxide. The decomposition of barium chlorite takes place according to the equation :

$$Ba(ClO_2)_2 = BaCl_2 + 2O_2 + 48{\cdot}6 \text{ kg.-cal.}$$

From this follows the equation :

$$Ba + Cl_2 + 2O_2 = Ba(ClO_2)_2(\text{solid}) + 148 \text{ kg.-cal.}$$

and

$$BaCl_2 + 2O_2 = Ba(ClO_2)_2 - 48{\cdot}6 \text{ kg.-cal.}$$

$$Ba(ClO_2)_2 + O_2 = Ba(ClO_3)_2 + 22{\cdot}8 \text{ kg.-cal.}$$

$$Ba(ClO_3)_2 + O_2 = Ba(ClO_4)_2 + 30{\cdot}2 \text{ kg.-cal.}$$

Consequently in compounds containing chlorine in different degrees of oxidation the formation is the less endothermic or the more exothermic the higher the degree of oxidation (Bruni and Levi, Gazzetta, 1915, **45**, ii, 161).

Barium chlorate, $Ba(ClO_3)_2$. Dry $Ba(OH)_2$ does not absorb chlorine, but in presence of water it rapidly takes it up, forming first hypochlorite and chloride, the former of which breaks up into chlorate and chloride,

$$6BaO + 6Cl_2 = 5BaCl_2 + Ba(ClO_3)_2$$

(Konigel-Wiesberg, Ber. 1879, **12**, 346).

As it is difficult to separate from the chloride, the chlorate is best prepared by neutralising a solution of chloric acid with barium carbonate and evaporating to the crystallising point. It crystallises in colourless monoclinic prisms with 1 mol. of water, soluble in 4 parts of cold and less than 1 part of boiling water.

If strongly heated fused barium chlorate be plunged into a jar of coal gas, a brilliant combustion of the carbon and hydrogen contained in the coal gas occurs at the expense of the oxygen of the chlorate.

Barium perchlorate, $Ba(ClO_4)_2,4H_2O$, is readily formed by neutralising perchloric acid with barium hydroxide or carbonate. It crystallises from the solution in long deliquescent prisms very soluble in water.

Barium bromide, $BaBr_2$, is formed on heating the dihydrate $BaBr_2,2H_2O$, which is prepared by saturating baryta water or barium carbonate or sulphide with hydrobromic acid; or by decomposing the sulphide with free bromine, sulphur being precipitated.

Another method is to bring together under water 12·5 parts of bromine and 1 part of amorphous phosphorus, by which a solution of hydrobromic and phosphoric acids is formed, which is neutralised with barium carbonate rendered alkaline by baryta water. The insoluble barium phosphate may then be filtered off and the bromide obtained by evaporation and crystallisation.

Barium bromide is very soluble in water. It crystallises in monoclinic prisms $a:b:c=1{\cdot}4494:1:1{\cdot}656$ $\beta=113°\ 29\tfrac{1}{2}'$ (Magge, Jahrb. Min. 1898, **1**, 130) isomorphous with the chloride, but unlike the latter salt is soluble in strong alcohol. It loses one molecule of water at 75°, and the second at 120° (Beckmann, J. pr. Chem. 1883 [ii], **27**, 126), m.p. of anhydrous salt 847°.

The solubility of $BaBr_2$ is at 0°, 49·5 ; 20°, 51·0 ; 60°, 55·1 ; 100°, 60·0 g. per 100 g. of solution (Kremers, Pogg. Ann. 1858, **103**, 65). The heat of formation of $BaBr_2$ is 169·46 cals., of $BaBr_2,2H_2O$ 178·57 cals. (Thomsen, J. pr. Chem. 1877 [ii], **16**, 97).

Barium oxybromides. Two oxybromides have been prepared by Beckmann (*l.c.*).

$BaBr(OH),2H_2O$ resembles the corresponding oxychloride. $BaBr(OH),3H_2O$ was obtained by adding alcohol to mixed solutions of $BaBr_2$ and $Ba(OH)_2$.

Barium iodide, BaI_2. Anhydrous, sp.gr. 4·917, it forms four hydrates with 7, 6, 2, 1 mols. of water respectively. Barium iodide is formed when hydrogen iodide is passed over baryta at a red heat, a violent action attended with incandescence occurring. It is generally prepared by mixing barium monosulphide with a saturated solution of iodine in alcohol as long as sulphur is precipitated; the filtrate is then boiled rapidly to near dryness, redissolved in a little water and again evaporated, this time to dryness, preventing the access of air as much as possible by performing the operation in a glass bolt-head. On redissolving the mass in hot water and allowing to cool, slender needles separate having the composition $BaI_2,7H_2O$ (Croft, Chem. Gaz. (Lond.), 1856, 125; 1877, **10**, 1343). Beckmann confirmed this figure for crystals obtained by evaporation in air, but found 6, 3, and 2 mols. at higher temperatures of evaporation. These crystals are very deliquescent and readily soluble in alcohol. They lose 6 molecules of water at 125°, and the remainder at 150° (Beckmann, J. pr. Chem. 1883 [ii], **27**, 126). They decompose slowly at ordinary temperatures, and quickly when warmed, giving off violet vapours of iodine. Commercial barium iodide crystallises at the ordinary temperature in large hexagonal prisms, apparently isomorphous with $SrCl_2,6H_2O$. They melt in their water of crystallisation at 25·7° (Centr. Min. 1918, 105). Magge (*l.c.*) obtained crystals in the monoclinic system isomorphous with $BaBr_2,2H_2O$.

The saturated solution of the double iodide of barium and mercury has a sp.gr. of 3·588, higher than that of Thoulet's solution, and may be of use for petrographical purposes (Rohrbach, Jahrb. Min. 1883, **2**, Mem. Brefliche Mittheilungen, 186).

Barium oxyiodide. Beckmann (J. pr. Chem. 1883 [ii], **27**, 126) prepared an oxyiodide of barium of the formula $BaI(OH),4H_2O$, which crystallises in short thick needles.

Barium iodate, $Ba(IO_3)_2$, is largely used for the preparation of iodic acid, and is obtained as a white granular precipitate by adding potassium iodate to barium chloride.

It is soluble in 3,000 parts of cold and 600 parts of boiling water. It dissolves in hot nitric acid, and crystallises out on cooling in bright, glittering, monoclinic prisms isomorphous with the chlorate. Hydrochloric acid dissolves it with evolution of chlorine.

Barium periodate. By passing iodine vapour in a current of dry air over heated oxide of barium a basic periodate of the formula $Ba_5I_2O_{12}$ or $Ba(IO_4)_2{\cdot}4BaO$ is formed. The same basic periodate is formed when barium iodate is heated to a high temperature:

$$5Ba(IO_3)_2 = Ba_5I_2O_{12} + 4I_2 + 9O_2$$

or on heating barium iodide in a current of air until no more iodine is given off:

$$5BaI_2 + 6O_2 = Ba_5I_2O_{12} + 4I_2$$

Hence Suguira and Cross (J. Chem. Soc. 1879, 118) conclude that $Ba_5I_2O_{12}$ is the most stable combination of barium, iodine, and oxygen.

Barium fluoride, BaF_2 (m.p. 1,289°), is obtained by neutralising hydrofluoric acid with barium hydroxide or recently precipitated carbonate; or by precipitating a solution of barium nitrate with sodium or potassium fluoride. It forms a white, granular, crystalline powder, sparingly soluble in water, but readily soluble in nitric, hydrochloric or hydrofluoric acids. It crystallises in the cubic system.

It combines with fluorides of silicon and boron, forming the silicofluoride, $BaF_2{\cdot}SiF_4$, and borofluoride, $BaF_2{\cdot}BF_3$, respectively. The former is precipitated by adding hydrofluosilicic acid to soluble barium salts as a crystalline precipitate totally insoluble in alcohol, and serves as a means of separating barium from strontium and calcium, which are not precipitated by hydrofluosilicic acid.

Barium fluoride forms a crystalline compound with the chloride of barium $BaCl_2{\cdot}BaF_2$, when a solution of barium chloride is mixed with one of sodium or potassium fluoride; this double compound is more stable than the fluoride itself, and remains as a granular mass on evaporation of the solution. The crystals are tetragonal in habit, and optically negative, m.p. 1,008°, sp.gr. 5·931.

Fuseya, Mori and Imamura (J. Soc. Chem. Ind. Japan, 1933, **36**, 175) state that the m.p. curve of MgF_2, BaF_2 indicated no compound, but there is a eutectic at 912° and 30–35% MgF_2. The m.p. curve of CaF_2,BaF_2 showed solid solution with a minima, m.p. 1,277° and 50% BaF_2.

Barium carbide, BaC_2, was first obtained by Maquenne (Ann. Chim. Phys. 1893 [vi], **28**, 263) by heating a mixture of the carbonate and carbon with magnesium or by the action of carbon on the amalgam in an atmosphere of hydrogen at a red heat. Moissan (Compt. rend. 1897, **118**, 683) obtained it in a pure crystalline condition by heating a mixture of the carbonate or the oxide with carbon in an electric furnace. Its specific gravity is 3·75, and it possesses properties similar to CaC_2, but is more fusible.

By heating barium oxide with carbon or in a stream of methane in a porcelain boat, barium carbide results according to equation

$$BaO + 3C = BaC_2 + CO$$

or

$$BaO + 3CH_4 = BaC_2 + CO + 6H_2$$

and at the comparatively low temperature of 1,000°–1,200°; the best temperature is about 1,150°, but pressure affects results. If the reaction is effected in an atmosphere of nitrogen the cyanide is produced (Fischer, with Bangert, Brennstoff-Chem. 1928, **9**, 328).

$$BaO + 3C + N_2 = Ba(CN)_2 + CO$$

The equilibrium pressure for the system

$$BaO + 3C \rightleftarrows BaC_2 + CO$$

was found to depend on temperature, percentage of carbide and ratio of BaO to C, indicating that the three solids must form a solid solution. Consistent pressure phases were obtained at 1,141°, 1,295°, with probable dissociation at 1,375° (Thompson, Amer. Electrochem. Soc. Sept. 1928).

A very porous variety of carbide which is decomposable by water vapour is made as follows: A mixture of barium carbonate or barium oxide with carbon and an inert insoluble material such as barium bi-silicate (which can be added also during the reduction process) is heated in a current of hydrogen or a mixture of carbon monoxide with excess of hydrogen (Ind. & Chem. Co. Canada, F.P. 682479).

Barium carbonate, $BaCO_3$. The native carbonate was first found at Leadhills in Scotland, in 1783, by Withering, and hence received the name *witherite, q.v.*

Knop (Landw. Versuchs-Stat. 1874, **17**, 65) found 0·02% of barium carbonate in Nile mud from Minich and Achmin; and Dworzack (*ibid., idem*) found baryta in the ash of the wheat grown thereon. *Alstonite*, $(BaCa)CO_3$, contains barium and calcium in varying proportions and is isomorphous with witherite. *Baryto-calcite*, $BaCO_3{\cdot}CaCO_3$ (*q.v.*), crystallises in the monoclinic system.

Boeke (Jahrb. Min. 1912, 9–10) shows by heating barium carbonate under pressure of carbon-dioxide that it undergoes two reversible transformations. At 811° the ψ form (witherite, orthorhombic and pseudo-hexagonal) passes to the β form (hexagonal), and at 982° to the α form (cubic), m.p. about 1,740° (Chem. Zentr. 1913, 1909). The system barium carbonate–calcium carbonate (represented by the minerals alstonite and baryto-calcite) give iso-dimorphous mixed crystals with a eutectic at 1,139° and 52½ mol. % $CaCO_3$. Up to 30 mol. % $CaCO_2$ the orthorhombic alstonite is the stable form, but with more calcium carbonate this is replaced by trigonal baryto-calcite. Monoclinic baryto-calcite is not present in the fusions.

Barium carbonate is rapidly formed when baryta, hydrated or anhydrous, is exposed to the atmosphere. When BaO is heated in CO_2 it absorbs the gas, becoming incandescent; the basic carbonate being formed (Raoult, Compt. rend. 1881, **92**, 110). It is readily prepared by precipitating aqueous solutions of the nitrate or chloride with ammonium carbonate, filtering and washing with hot water; or by igniting a mixture of 10 parts powdered heavy-spar, 2 parts charcoal, and 5 parts pearl ash (potassium carbonate), potassium sulphide and barium carbonate are obtained and may be separated by water. The impure carbonate thus produced may be used to prepare other salts of barium, but these salts will contain iron.

Artificial barium carbonate is a dense soft white powder, poisonous and hence used for destroying rats. It is very sparingly soluble in water, slightly soluble in water containing carbonic acid, owing to the formation of an acid carbonate which is stable only in solution. It dissolves readily in ammonium chloride, nitrate and succinate, and when boiled with ammonium chloride is totally decomposed, forming ammonium carbonate and barium chloride.

The solubility of $BaCO_3$ in water has been determined by Weissenberger (Z. physikal. Chem. 1914, **88**, 257), and also in water containing small quantities of sodium hydroxide, which represses the hydrolysis and so furnishes a lower and more accurate value for the solubility. The minimum solubility is found in aqueous solutions containing $1{\cdot}25\times10^{-5}$ mols. of sodium hydroxide. The following values were obtained (1) for pure water at 13°, $1{\cdot}62\times10^{-3}$; 18°, $1{\cdot}72\times10^{-3}$; 22°, $1{\cdot}83\times10^{-3}$; 27°, $1{\cdot}96\times10^{-3}$; 33°, $2{\cdot}14\times10^{-3}$; 37°, $2{\cdot}28\times10^{-3}$ mols. per litre, and (2) true values calculated from experimental results in faintly alkaline solutions at 14°, $4{\cdot}32\times10^{-4}$; 18°, $4{\cdot}57\times10^{-4}$; 23°, $4{\cdot}89\times10^{-4}$; 27°, $5{\cdot}22\times10^{-4}$; 32°, $5{\cdot}69\times10^{-4}$; 38°, $6{\cdot}27\times10^{-4}$ g. mol. per litre.

O. Haehnel (J. pr. Chem. 1924 [ii], **108**, 187–193) finds that the solubility of $BaCO_3$ in water containing CO_2 is at 1 atm. 0·27%, at 25 atm. 0·59%.

Barium carbonate is not decomposed at a strong red heat, but at 1,361° it fuses with loss of carbon dioxide; the tension of CO_2 emitted at 1,100° is 20 mm.; at 1,600° dissociation is complete. The decomposition is much more easily effected in presence of carbon, being complete at 1,450°. It is decomposed by steam at a red heat, and very easily if mixed with an equal weight of chalk or slaked lime.

The artificial carbonate is used extensively in chemical analysis.

Barium nitride, Ba_3N_2. Maquenne (Bull. Soc. chim. 1892 [iii], **7**, 368) prepared this compound by passing nitrogen into a tube containing a 25% barium amalgam at a red heat. Guntz and Mentrel (*ibid.* 1903 [iii], **29**, 581) obtained it by heating barium ammonium at 430°. The product is a light porous material of a canary-yellow colour, and decomposes water in the cold, giving ammonia and $Ba(OH)_2$.

The pure nitride and hydride are readily obtained by heating the metal in the respective gases. When the nitride is heated in a current of hydrogen a compound having the formula $B_3N_2H_4$ is formed, but the process is incomplete, since the compound reacts even at relatively low temperatures with hydrogen according to the equation

$$Ba_3N_2H_4+H_2=3BaH_2+N_2$$

When hydrogen is passed over the heated impure nitride ammonia is formed. BaH_2 which is thereby produced is readily transformed back to the nitride by the action of nitrogen, so that a process is given for the fixation of nitrogen (F. W. Dafert and R. Miklauz, Monatsh. 1913, **34**, 1685).

Barium ammonium is formed by the action of ammonia gas on barium or barium amalgam below 28°; but it is best prepared by dissolving barium in dry liquid ammonia at −50°, when it forms a dark blue oily liquid immiscible with the liquid ammonia. The product is somewhat indefinite, but appears to contain the compound barium hexammine, $Ba(NH_3)_6$.

Barium amide, $Ba(NH_2)_2$, is obtained by heating barium ammonium to 60° or by passing ammonia over barium at 280°C.

When a barium salt and excess of potassamide are allowed to interact in liquid ammonia solution a white insoluble precipitate of potassium ammonobariate, $BaNK,2NH_3$ or $Ba(NH_2)_2,KNH_2$, is produced. The strontium and calcium salts may be prepared in a similar manner (Franklin, J. Amer. Chem. Soc. 1915, **37**, 2295).

Barium azide, BaN_6, is prepared by adding ammonia water to a solution of barium hydroxide and heating the mixture with ammonium azide (Berthelot and Matignon, Bull. Soc. chim. 1894 [iii], **11**, 744; Ann. Chim. Phys. 1894 [vii], **2**, 144). The excess of barium hydroxide is removed by passing carbon dioxide into the liquid, and the filtrate is evaporated *in vacuo* or over sulphuric acid. The compound crystallises in the monoclinic system and belongs to one of the space groups $C_{2}^{1}h$ or $C2/2h$. The elementary cell contains 10 mols., $a=6{\cdot}22$, $b=29{\cdot}29$, $c=7{\cdot}02$Å, d (X-ray) $2{\cdot}9365\pm0{\cdot}0025$ (Günther, Porger, Rosbaud, Z. physikal. Chem. 1930, B. **6**, 459).

Günther and associates (Z. Elektrochem. 1930, **36**, 211) show that the thermal decomposition of barium azide starts by the reaction $BaN_6=Ba+3N_2$, the metal formed then reacting with unchanged azide to give nitride, $Ba+2BaN_6=Ba_3N_2+5N_2$. It is this latter reaction which is responsible for the explosive character of the decomposition, the former reaction being only feebly exothermic. Harvey (Trans. Faraday Soc. 1933, **29**, 653) states that for the temperature range of 100°–130° an induction period is observed similar to that in the case of Hg fulminate. The final product of decomposition seems to be mixed crystals of nitride with 25% or more of free metal. If the azide is decomposed slowly in the presence of oxygen the metal nuclei are oxidised and little nitride is formed. X-rays decompose the azide slowly with the direct formation of nitride. Barium azide is used in the manufacture of the barium-coated cathodes of radio-valves.

Barium nitrite, $Ba(NO_2)_2,H_2O$, is prepared by heating the nitrate above its m.p., dissolving the residue in water, precipitating any baryta formed by passing a stream of carbon dioxide through the solution, adding alcohol to the filtrate to precipitate the unreduced nitrate and evaporating to the crystallising point. Or by passing nitrous vapours into baryta water, evaporating to dryness, digesting in a small quantity of water (not sufficient to dissolve the nitrate) and crystallising. The pure compound is most readily prepared by adding barium chloride to a boiling solution of silver nitrite, filtering off the silver chloride, and evaporating. It is permanent in the air, readily soluble in water or alcohol, and crystallises in colourless prisms, either needle-shaped or, according to Fischer (Pogg. Ann. 1849, **77**, 115), in thick short prisms.

Barium nitrate, $Ba(NO_3)_2$. A native barium nitrate has been discovered in Chile in the form of colourless octahedra, occasionally twinned like spinel (Groth, Jahrb. Min. 1883, **1**, Ref. 14).

Barium nitrate is prepared on the large scale either by dissolving the native carbonate (witherite) or the crude sulphide in dilute nitric acid, or by mixing hot saturated solutions of barium chloride and sodium nitrate. On cooling, the larger portion of the barium nitrate crystallises out, and the evaporation of the mother liquors yields the remaining portion.

Manufacture (F.P. 636331).—100 kg. commercial barium sulphide, BaS, 88·7% pure, is mixed with 81·2 kg. NH_4NO_3 and 7 litres water. The nitrate, $Ba(NO_3)_2$, thus obtained is free from sulphur.

The reaction

$$BaSO_4+Ca(NO_3)_2\rightleftharpoons Ba(NO_3)_2+CaSO_4$$

is a reversible one, but by employing an excess of calcium nitrate (2 mols.) fusing the substances together, and then suddenly cooling the heated mass, about 75% of the $BaSO_4$ is converted into Ba nitrate, which rapidly crystallises from the excess of $Ca(NO_3)_2$ when the product is dissolved (Hans Kühne, D.R.P. 248524, 1912).

Barium nitrate crystallises in lustrous, colourless, regular octahedra, frequently modified by faces of the cube, it has sp.gr. 3·2. The crystals are permanent in the air, decrepitating when heated and melting at 595·53° (Carnelley 597°). At a red heat the salt decomposes, evolving oxygen, nitrogen and nitrogen peroxide, and leaving a residue of pure baryta. It detonates slightly with combustible bodies and decomposes with a yellowish light when thrown upon the fire. It is largely used in pyrotechny, especially for the preparation of green fire.

It dissolves in water, producing a slight depression of temperature; 100 parts of water dissolve 5·2 parts of barium nitrate at 0°, 9·2 at 20°, 17·1 at 50°, and 32·2 at 100°. It is less soluble in dilute nitric acid; hence a second crop of crystals may be obtained from cooled saturated solutions on addition of a little nitric acid. It is quite insoluble in concentrated nitric acid and in alcohol.

Hirzel (Zeitsch. f. Pharm. 1854, 49) obtained a hydrate, $Ba(NO_3)_2,2H_2O$, from a solution cooled below 12°. Berry (Chem. News, 1881, **44**, 190), by saturating the same water with barium and strontium nitrates, introducing a crystal of $Sr(NO_3)_2,4H_2O$, and evaporating over sulphuric acid *in vacuo*, obtained crystals of a double nitrate containing 17% of a hydrated barium nitrate isomorphous with the strontium compound. On account of the great electro affinity of nitrion (nitrate ion), the formation of double nitrates is rare, and with one exception (the double nitrate of barium and potassium) they are formed only when one of the metals has a valency greater than 2. The unexpected formation of the double nitrate of potassium and barium was first observed by Wallbridge (J. Amer. Chem. Soc. 1908, **30**, 154), whose analysis showed it to be the anhydrous salt

$$2KNO_3,Ba(NO_3)_2$$

Foote showed (*ibid.* 1910, **32**, 251) that the double salt can form at 25° under a moderately wide range of conditions as, for example, from solutions containing 15 to 27% KNO_3, and from 6 to 2% $Ba(NO_3)_2$. The salt cannot be recrystallised. Only one well-defined basic nitrate, $Ba_2N_2O_7$, is known, and this forms several hydrates.

No basic nitrates of Ba or Sr are formed at 25° similar to the Ca compound

$$CaO,Ca(NO_3)_2,3\tfrac{1}{2}H_2O$$

(Parsons and Corson, J. Amer. Chem. Soc. 1910, **32**, 1383).

Barium monosulphide, BaS, is obtained in a pure state by passing hydrogen sulphide over heated baryta as long as water is formed. Veley (J.C.S. 1886, **49**, 369) prepared the hydrate of barium hydroxide,

$$Ba(OH)_2,8H_2O,$$

which, heated at 80° in a current of hydrogen, yielded the monohydrate,

$$Ba(OH)_2,H_2O,$$

and this on treatment with hydrogen sulphide gave BaS and water:

$$Ba(OH)_2,H_2O+H_2S=BaS+3H_2O$$

It may also be prepared by passing carbon disulphide over red-hot baryta, or by reducing powdered barium sulphate in a stream of hydrogen.

On the manufacturing scale it is prepared by roasting 100 parts of heavy-spar with 20 parts of coal slack or charcoal. If charcoal is used, a thorough mixture must be effected, as the reaction is otherwise very imperfect, owing to the non-fusibility of the mass. If the slack of bituminous coal is used, the " caking " supplies a carbonaceous material which readily permeates the mass and ensures complete reduction. The admixture of resin, oil, or sawdust is also advantageous, and the asphalt of gasworks is a valuable reducing material, as the hydrogen contained in it prevents the formation of polysulphides of barium. From the mass thus obtained containing excess of carbon and some undecomposed sulphate, the sulphide is extracted by treatment with hot water.

Another method is to heat a mixture of 100 parts heavy-spar, 200 of common salt, and 15 parts charcoal powder in a reverberatory furnace, the salt being added to assist fusion.

4–6 parts low-grade barium sulphate ore containing preferably more than 4% silica, in a finely powdered condition, is mixed with 1 part of powdered coal and some binding material is pressed into cakes or briquettes and heated in a furnace until the sulphate changes to sulphide (U.S.P. 1685722 of 10/11/24).

Reducing gases for reducing the sulphate are better than coal. For commercial purposes the best results are obtained with water gas at 600°–625°, when $BaSO_4$ gives BaS and a trace of oxide and thiosulphate (L. Marino, Gazzetta, 1913, **43**, 416–422).

Wells (Ind. Eng. Chem. 1916, **8**, 770) found that the maximum reduction of barium sulphate to water-soluble barium sulphide, 96–97%, was obtained at temperature above 1,000° with 15–16% carbon. The operation gave the highest efficiency in an externally fired furnace ; with an internally fired furnace insoluble compounds were produced in larger quantity. The mol. heat of formation of BaS is 102·5 kg.-cal (Sabatier), of BaS aq. is 107·8 kg.-cal. (Thomsen); the mol. heat of solution of BaS is 7·3 kg.-cal. (Sabatier).

Barium sulphide forms a white mass of hepatic odour and alkaline taste, soluble in water, forming a mixture of hydrate and sulphydrate:

$$2BaS+2H_2O=Ba(SH)_2+Ba(OH)_2$$

When exposed to the air it becomes converted into carbonate with evolution of hydrogen sulphide, owing to absorption of moisture and carbon dioxide. When heated to redness in presence of aqueous vapour, it is converted into barium sulphate with elimination of hydrogen. It is decomposed by hydrochloric and nitric acids with formation of the chloride and nitrate and elimination of hydrogen sulphide. Chlorine, bromine, and iodine decompose it with formation of chloride, bromide, and iodide, and deposition of sulphur.

The phosphorescent material known as " Bolognian phosphorus " is a sulphide of barium obtained by heating 5 parts of precipitated barium sulphate with 1 part of powdered charcoal over a gas flame for half an hour, and then heating for 10 minutes over the blowpipe ; it must be sealed up while still hot in glass tubes. After exposure to the sun's rays, or to any light rich in ultra-violet rays such as that emitted by burning magnesium wire or the electric arc, it phosphoresces in the dark with a brilliant orange-coloured light. Sulphides of barium, strontium and calcium are now manufactured for the preparation of luminous paints (*q.v.*). Barium sulphide is now largely used in the manufacture of *lithopone* by adding it dissolved in water to a solution of zinc sulphate. Mutual precipitation takes place, and the white powder formed, consisting of zinc sulphide and barium sulphate, is used as a rubber filler and pigment.

When a solution of 5 parts of barium sulphide is boiled with 1 part of sulphur, and the solution evaporated over sulphuric acid *in vacuo*, colourless six-sided transparent tabular crystals of $BaS,6H_2O$ are deposited, which are decomposed by a small quantity of water, forming barium hydrosulphide, which dissolves, and barium hydroxide, which remains undissolved.

Barium hydrosulphide, $Ba(SH)_2$, is formed by saturating a warm solution of barium hydroxide or sulphide with hydrogen sulphide, evaporating apart from the air and cooling, when crystals of baryta and yellow prisms separate out. The mother liquor is mixed with alcohol, filtered from the precipitated sulphur and barium thiosulphate and cooled to −10°, when colourless, transparent four-sided prisms of the hydrosulphide are obtained. The crystals contain water, which they lose on heating, becoming white; they decompose, with efflorescence, in the air, forming barium thiosulphate and sulphate. Heated in a retort, they lose their water of crystallisation without fusing, evolving hydrogen sulphide as the temperature approaches redness, and leaving a yellow mass of barium monosulphide, which becomes white on cooling. It is insoluble in alcohol.

Veley (J.C.S. 1886, **49**, 369) finds that the composition of crystals of barium hydrosulphide is $Ba(SH_2),4H_2O$.

Barium trisulphide, BaS_3, is formed as a greenish-yellow mass when 2 parts of barium sulphide are fused with 1 part of sulphur, the excess of sulphur being distilled off below 360°. It melts at 400° with loss of sulphur and formation of a black liquid. On boiling for some time with water it dissolves to a red liquid which deposits on cooling crystals of the hydrated mono- and tetrasulphides of barium.

Barium tetrasulphide, BaS_4. When 7 parts of barium sulphide are boiled in water with 4 parts of sulphur, pale-red rhombic prisms are deposited, dissolving in water to a red-coloured liquid from which alcohol precipitates it as an orange-coloured crystalline powder.

Veley (*l.c.*) obtained it by dissolving sulphur in a warm saturated solution of barium hydrosulphide; the crystals which separate have the composition $BaS_4,2H_2O$.

When a mixture of 2 parts of barium hydroxide, 1 part of sulphur, and 25 parts of water is boiled, a deep brown liquid is obtained, which on cooling becomes orange-red in colour. If this solution is evaporated rapidly until a crust is formed on the surface, the liquid on cooling deposits large red prisms of barium tetrasulphide, $BaS_4{\cdot}H_2O$, mixed with sulphur and barium thiosulphate. The orange-red liquid contains sulphur and barium in the proportion corresponding with the pentasulphide, which appears to exist in solution, but decomposes during evaporation (Compt. rend. 1866, **63**, 390).

Barium pentasulphide, BaS_5, is obtained in solution by boiling an aqueous solution of the monosulphide with sulphur. On evaporation of the caustic alkaline yellow solution, crystals of barium tetrasulphide and sulphur are obtained: $BaS_5 = BaS_4 + S$.

Barium thiocarbonate, $BaCS_3$, is deposited as a canary-yellow crystalline powder when a solution of barium sulphide is added to carbon disulphide (Thenard, Compt. rend. 1874, **79**, 673). On the large scale 90% yields may be obtained, and Dumas suggested its use against the phylloxera in wine districts. Thenard was of opinion that this barium salt would be injurious to the soil, and proposed to convert it into the potassium salt by adding potassium sulphate to its solution.

Barium sulphite, $BaSO_3$, is obtained as a white crystalline precipitate by adding potassium or sodium sulphite to a soluble barium salt. It is soluble in a warm solution of sulphurous acid, and crystallises out on cooling in six-sided prisms. When heated in closed vessels it is converted into a mixture of sulphide and sulphate, but when heated in air the sulphate is the sole product. Birnbaum and Wittich (Ber. 1880, **13**, 651) state that BaO unites slowly with SO_2 at 200°, but more rapidly at 230°, forming $BaSO_3$.

Barium sulphate, $BaSO_4$, occurs in nature as *baryte* (*q.v.*), or heavy-spar, forming large tabular crystals belonging to the rhombic system.

Crystals of artificial baryte, identical in form and properties with native heavy-spar, may be obtained by fusing certain metallic chlorides, such as those of manganese, sodium, potassium, or even barium itself, gradually dissolving barium sulphate in the fused mass, very slowly cooling and afterwards extracting the soluble chlorides with water. By this means Gorgeu (Compt. rend. 1883, **96**, 1734) prepared crystals much larger than those obtained by the older process of fusing potassium sulphate with barium chloride.

Cooper Fuller and Klein (J. Amer. Chem. Soc. 1911, **33**, 845) obtained crystals 5 mm. long and 1 mm. wide, resembling natural baryte, by crystallisation from fused admixture of barium chloride and sodium sulphate.

The sp.gr. of the mineral and of the artificial crystals varies from 4·3 to 4·7.

Barium sulphate has been formed by Spring (Bull. Soc. chim. 1885 [ii], **44**, 166) by subjecting an intimate mixture of molecular proportions of sodium sulphate and barium carbonate to great pressure. It is precipitated as a heavy white amorphous powder of sp.gr. 4·0–4·5, when sulphuric acid or a soluble sulphate is added to the solution of a barium salt; this precipitate is nearly insoluble in water (1 part in 232,588 parts), very slightly soluble in dilute acids, more so in strong acids. When freshly precipitated, it is readily soluble in concentrated sulphuric acid at 100°, the solution depositing on cooling lustrous prisms of the *acid barium sulphate* $BaH_2(SO_4)_2$. If the acid solution be exposed to the air, moisture is taken up, and silky needles of a salt having the composition

$$BaH_2(SO_4)_2,2H_2O$$

are deposited. Both these acid salts are decomposed by water, yielding sulphuric acid and the neutral salt.

The solubility of $BaSO_4$ in 97·86% sulphuric acid at 25° was found to be 14·91 g. in 100 c.c. acid. The saturated solution contained $BaSO_4{\cdot}H_2SO_4$. By electrolytic transport the compound can be accumulated in the anode compartment where it crystallises. A barium selenic acid also exists, $BaSeO_4,H_2SeO_4$, which can be similarly concentrated and deposits crystals (Trenner and Taylor, J. Physical Chem. 1931, **35**, 1336). Concentrated sulphuric acid does not attack anhydrous baryta, but pyrosulphuric acid attacks it so violently that the mass becomes incandescent, and forms barium sulphate. For heat of combinations of Ba and SO_4 ions, *see* J. A. Muller, Bull. Soc. chim. 1918 (iv), **23**, 13.

Barium sulphate is also soluble to a perceptible extent in ammonium and potassium nitrates. Hydrobromic acid solution containing 40% HBr dissolves it to the extent of 1 in 2,500 parts acid (Haslam, Chem. News, 1886, **53**, 87; Karaoglanov, Z. anal. Chem. 1917, **56**, 225).

Barium sulphate is partially decomposed by boiling with a concentrated solution of a fixed alkaline carbonate into alkaline sulphate and barium carbonate, but the reaction is complete if the sulphate and alkaline carbonate are fused first together; if mixed with carbon it is reduced to the sulphide (*q.v.*).

Powdered heavy-spar is used to adulterate white lead, but has not sufficient body to form a pigment by itself; the amorphous sulphate is prepared on the large scale by precipitation of a solution of barium chloride of sp.gr. 1·19 by one of sulphuric acid of sp.gr. 1·245, and is used as a pigment under the name of "permanent white" or "blanc fixe." In America it is prepared on a large scale by grinding the mineral, after which the pulp is classified and the cream-coloured mud treated with sulphuric acid to remove iron compounds.

Barium sodium sulphate, $BaNa_2(SO_4)_2$, is formed as an opaque hard mass of pearly lustre by fusing together equivalent quantities of the sulphates of sodium and barium (Berthier).

Barium pyrosulphate, BaS_2O_7. If precipitated barium sulphate be dissolved in fuming sulphuric acid, and the solution heated to 150°, on cooling a glistening deposit of granular crystals of the pyrosulphate is obtained. Decomposition of these crystals occurs at a low red heat without previous fusion.

Barium dithionate, $BaS_2O_6,2H_2O$, is prepared by adding barium sulphide to the manganese salt formed on passing sulphur dioxide through finely divided manganese dioxide suspended in water:

$$MnS_2O_6+BaS=MnS+BaS_2O_6$$

On allowing the solution to evaporate in a warm place, glittering crystals of the salt $BaS_2O_6,2H_2O$, are deposited. According to V. Lang (Sitzungsber. 1862 [2], **45**, 27), they are monoclinic, of prismatic habit $a:b:c=0{\cdot}9343:1:1{\cdot}4030$ $\beta=110°\ 37'$.

The crystals are soluble in 4 parts of water at 18° and in 1·1 parts at 100°. When the dry salt is heated, it breaks up into sulphur dioxide and barium sulphate. The same decomposition occurs on boiling with hydrochloric acid, but the solution of the dithionate itself in water may be boiled without decomposition.

A tetrahydrate, $BaS_2O_6,4H_2O$, in distinct shining monoclinic crystals, may also be obtained by spontaneous evaporation. These effloresce on exposure to air.

Barium thiosulphate,

$$BaS_2O_3,H_2O \text{ or } BaH_2(SO_2)_2,$$

is obtained as a white crystalline precipitate when the sodium salt $Na_2S_2O_3$ is added to barium acetate solution; it loses its water of crystallisation at 215°. The anhydrous salt, when heated to redness, gives off sulphur and leaves a residue consisting of barium sulphide, sulphite and sulphate:

$$6BaS_2O_3=BaS+2BaSO_3+3BaSO_4+6S.$$

Barium selenide, $BaSe$, is formed by heating barium selenite to redness in a stream of hydrogen. It is decomposed by water into barium hydroxide and a higher selenide, which is decomposed by acids with evolution of H_2Se and precipitation of selenium.

Barium selenite, $BaSeO_3,H_2O$, obtained by dissolving the carbonate in selenious acid, can be heated to whiteness without decomposition, and at the same temperature the selenate is converted into the selenite.

Barium selenate, $BaSeO_4$, resembles the sulphate in being insoluble in water, but differs from it in being decomposed by boiling hydrochloric acid with evolution of chlorine into selenite, which dissolves in the hydrochloric acid.

Barium chromate, $BaCrO_4$, is precipitated as a yellow crystalline powder when potassium chromate or bichromate is added to the solution of a barium salt. The salt may be obtained in green rhombic crystals isomorphous with $BaSO_4$ by heating two equivalents of $BaCl_2$ with one equivalent of potassium chromate and one of sodium chromate, and allowing the mixture to cool; the chlorides may be boiled out with water, leaving the right rhombic prisms of $BaCrO_4$, of sp.gr. 4·6. They are insoluble in water, but are easily soluble in hydrochloric and nitric acids, and are decomposed by sulphuric acid into $BaSO_4$ and CrO_3 (Bourgeois, Compt. rend. 1879, **88**, 382).

The precipitated chromate is used as a pigment under the name of "lemon yellow" or "yellow ultramarine." When strong sulphuric acid is added to the dry pigment, great heat is developed, and it is coloured deep red from liberation of CrO_3. If it be now ground in a mortar and heated to bright redness, the chromic acid is reduced to chromic oxide, and a fine green pigment is obtained (Douglas, Chem. News, 1879, **40**, 59).

Barium dichromate, $BaCr_2O_7$, is obtained by dissolving barium chromate in hot concentrated chromic acid. On cooling, red crystals of the composition $BaCr_2O_7,2H_2O$ are deposited, which lose their water at 100°, and are decomposed by water into the normal chromate and chromic anhydride (Preis and Rayman, Ber. 1880, **18**, 340).

Barium manganate, $BaMnO_4$, formed when manganese dioxide is heated with barium carbonate or nitrate, is an emerald-green powder consisting of microscopic four-sided prisms or six-sided plates, insoluble in water but decomposed by acids. This salt is used as a pigment under the name of *manganese green* or *Cassel green.*

Barium manganate may be prepared according to Schlesinger and Siems (J. Amer. Chem. Soc. 1924, **46**, 1965) by the gradual addition of a saturated solution of potassium permanganate to a boiling saturated solution of barium hydroxide, carbon dioxide being excluded. The bluish-black barium manganate is washed by decantation, separated, dried at 110°, and then over phosphoric pentoxide.

Barium permanganate, $Ba(MnO_4)_2$, is prepared by passing carbon dioxide through water containing barium manganate in suspension; after filtering off the barium carbonate the red solution is rapidly evaporated. It may be obtained by the action of barium chloride on silver permanganate; or potassium permanganate may be decomposed by slight excess of hydrofluosilicic acid, the mixture kept cool, and, after separation of the precipitated potassium silicofluoride, the supernatant solution decanted and saturated in the cold with barium hydroxide. After separation of the insoluble barium silicofluoride, the solution is evaporated until the barium permanganate separates out on cooling (Rousseau and Bruneau, Compt. rend. 1884, **98**, 229). It forms large orthorhombic octahedra, deep-red and almost black, with a violet reflection, and is used for the preparation of permanganic acid and of the ammonium salt.

Barium manganite.—Rousseau and Saglier (Compt. rend. 1884, **99**, 139) find that on heating 2 g. of barium manganate with 10 g. of barium chloride for 4 hours at 1,500° and extracting with water and dilute acid, a residue of small opaque bluish-black crystals of *barium manganite*, $BaMnO_3$, remains ; sp.gr. 5·85 ; readily soluble in hydrochloric acid with evolution of chlorine. The manganite is also formed when mixtures of manganese chloride and barium oxychloride are heated below 1,000° or above 1,100°. Between these temperatures the product is barium dimanganite,

$$BaO{\cdot}2MnO_2,$$

which crystallises in brilliant black lamellæ. At 1,500° the manganite is reconverted to manganate.

Barium phosphide, Ba_3P_2. When the vapour of phosphorus is passed over red-hot baryta, a brownish-red mixture of barium phosphide and phosphate is obtained, formerly known as "phosphuret of baryta." It is decomposed by water, forming a solution of barium hypophosphite and evolving a mixture of free hydrogen and spontaneously inflammable hydrogen phosphide.

Jaboin (Compt. rend. 1900, **129**, 762) prepared the phosphide by heating 100 parts of barium phosphate with 16 parts of lamp-black in an electric furnace. The product so obtained has a crystalline structure. It decomposes water, yielding PH_3 and $Ba(OH)_2$.

Barium monometaphosphate is obtained as a white powder by evaporating a solution of barium carbonate in excess of metaphosphoric acid and heating the residue to 316°. Its formula is not known with certainty.

Barium dimetaphosphate,

$$Ba(PO_3)_2,2H_2O,$$

is formed as a crystalline sparingly soluble precipitate when barium chloride is added to a solution of the corresponding ammonium or sodium salt (Fleitmann, Pogg. 1849, **78**, 254).

Barium trimetaphosphate,

$$Ba_3P_6O_{18},6H_2O,$$

apparently a polymeric form of the last salt, is produced when a solution of 1 part of the corresponding sodium salt in 10 to 15 parts of water is mixed with a nearly saturated solution of 3 parts barium chloride. On standing, the salt separates in monoclinic prisms, which give off two-thirds of their water at 100°, and the rest at a higher temperature (T. Fleitmann and W. Henneberg, Annalen, 1847, **65**, 313).

Barium hexametaphosphate, $Ba_3P_6O_{18}$, is obtained as a gelatinous precipitate by precipitating the corresponding sodium salt with barium chloride (Graham, Pogg. Ann. 1834, **32**, 68).

Monobarium orthophosphate,

$$BaH_4(PO_4)_2,$$

is prepared by evaporating a solution of the di- or tri-barium salt in aqueous phosphoric acid. It forms colourless crystals—triclinic according to Erlenmeyer—with acid reaction ; soluble without decomposition in a small quantity of water, but decomposed by excess of water into free phosphoric acid and the neutral salt.

Joly (Compt. rend. 1884, **98**, 1274) states that as the total weight of salt brought in contact with the same quantity of water increases in arithmetical progression, the weight which is dissolved without decomposition decreases in geometrical progression ; but as soon as half the original salt has been decomposed a diacid salt is formed, $BaO{\cdot}2P_2O_5+xH_2O$, the proportion of which increases as the acidity of the liquid increases and eventually exists alone in solution.

Dibarium orthophosphate, $Ba_2H_2(PO_4)_2$ or $BaHPO_4$, is obtained as a white, scaly, crystalline precipitate when hydrogen disodium phosphate is added to a neutral solution of a barium salt. It is soluble in 20,570 parts of water at 20°, somewhat more soluble in water containing barium or sodium chloride or ammoniacal salts. From the solution in nitric or hydrochloric acid excess of ammonia precipitates the tribarium salt or a salt intermediate between the two. Thus, according to Wackenroder, a solution of $BaHPO_4$ in nitric acid yields, on addition of ammonia, a precipitate of barium phosphato-nitrate,

$$4BaHPO_4{\cdot}Ba(NO_3)_2,$$

which leaves, on heating, a mixture of di- and tri-barium phosphates.

By precipitating a solution of dibarium phosphate with alcohol, a salt intermediate between the mono- and di- salts is obtained :

$$BaH_4(PO_4)_2{\cdot}2BaHPO_4,3H_2O$$

If a mixture of potassium silicate and baryta water is boiled, and afterwards mixed with a solution of potassium silicate containing a quantity of potassium phosphate, on cooling, cubical crystals of the composition $BaKPO_4,10H_2O$ separate out. $BaNaPO_4,10H_2O$ was similarly obtained in regular tetrahedra (de Schulten, Compt. rend. 1883, **96**, 706).

Tribarium orthophosphate or neutral phosphate of barium, $Ba_3(PO_4)_2,H_2O$, is prepared by adding hydrogen disodium phosphate to a solution of barium chloride rendered strongly alkaline by ammonia, and separates as a heavy granular powder. It parts with a portion only of its water at 200°.

If a saturated solution of tribarium phosphate in hydrochloric acid is evaporated, on cooling, crystals of barium chloride are deposited, monobarium phosphate being left in solution, and on further treatment with hydrochloric acid all the barium may be crystallised out as barium chloride, and pure phosphoric acid remains.

If the solution of tribarium phosphate in hydrochloric acid is boiled, shining needles form in the liquid, and on adding sufficient water to redissolve them, well-defined crystals of a phosphato-chloride, $4BaH_4(PO_4)_2{\cdot}BaCl_2$, are deposited on standing (Erlenmeyer, Jahresber. 1857, 147).

According to Ludwig, a solution of dibarium phosphate in hydrochloric acid also yields, on addition of ammonia, a phosphato-chloride containing $3Ba_5H_2P_4O_{16}\cdot BaCl_2,3H_2O$.

A salt intermediate between the di- and triphosphates, containing $Ba_3(PO_4)_2\cdot 2BaHPO_4$ or $Ba_5H_2P_4O_{16}$, is formed when a solution of the dibarium phosphate in hydrochloric acid is mixed with just sufficient ammonia to precipitate the salt.

Barium pyrophosphate, $Ba_2P_2O_7$. Pyrophosphoric acid does not precipitate barium salts, but gives with baryta water a precipitate of barium pyrophosphate. Barium salts, however, give with sodium pyrophosphate a white amorphous precipitate of barium pyrophosphate, soluble in aqueous pyrophosphoric and sulphurous acids ; more soluble in hydrochloric or nitric acid, but not perceptibly soluble in water containing ammonium chloride or in acetic acid.

Hans Winter (Diss., Leipzig, 1913) prepared the two apatites of the composition

$$BaCl_2,3Ba_3P_2O_8 \text{ and } BaF_2,3Ba_3P_2O_8,$$

in a crystallised condition, by fusing the phosphates and halogen salts together in an electric oven.

Monobarium arsenate, $BaH_4(AsO_4)_2$, is obtained by adding baryta water to aqueous arsenic acid until a precipitate begins to form, or by dissolving the dibarium salt in aqueous arsenic acid and leaving the solution to crystallise.

Dibarium arsenate,

$$2BaHAsO_4,H_2O \text{ or } BaHAsO_4,H_2O,$$

according to Berzelius, is obtained when a solution of the disodium salt is added to excess of barium chloride. It gives up its water at a red heat, and in contact with water is decomposed into the tribarium salt, which is precipitated, and the monobarium salt, which dissolves.

Tribarium arsenate, $Ba_3(AsO_4)_2$, is obtained as a white sparingly soluble powder by precipitating aqueous arsenic acid with baryta water, or better, by gradually dropping trisodium arsenate into barium chloride.

Barium ortho-thioarsenate, $Ba_3(AsS_4)_2$, is obtained together with $Ba(AsS_3)_2$ by the action of hydrogen sulphide on a solution of $BaHAsO_4$. The barium thioarsenate is precipitated by adding alcohol. Arsenic pentasulphide prepared by the action of a rapid stream of hydrogen sulphide on a solution of arsenic acid and hydrochloric acid, reacts with a freshly prepared solution of $Ba(SH)_2$ according to the equation

$$3Ba(SH)_2+As_2S_5=Ba_3(AsS_4)_2+3H_2S$$

After evaporation transparent yellow needles of $Ba_3(AsS_4)_2,6H_2O$ separate (E. Glatzel, Z. anorg. Chem. 1911, **70**, 86). In solution it reacts with potassium chloride yielding potassium barium orthothioarsenate $BaKAsS_4,6H_2O$, which may also be prepared directly by adding KCl to a solution of $Ba(SH)_2$ saturated with As_2S_5.

Barium silicides.—L. Wohler and W. Schiff (Z. anorg. Chem. 1932, **209**, 33) state that the mono-silicide $BaSi$ is obtained from the elements by brief heating at 1,000° and subsequent quenching. By heating at 1,200°–1,400° it is slowly converted into the disilicide $BaSi_2$. Ba also forms the compound $BaSi_3$. The heats of formation determined are $BaSi$ 181·5, $BaSi_3$ 399·2 kg.-cal.

Barium silicate.—The two compounds $BaSiO_3$ and Ba_2SiO_4 are described by Jander (Z. anorg. Chem. 1928, **174**, 11). But, according to Eskola (Amer. J. Sci. 1922, **4**, 331), the four compounds,

(1) $2BaO,SiO_2$
(2) BaO,SiO_2
(3) $2BaO,3SiO_2$ and
(4) $BaO,2SiO_2$

exist. Of these (3) and (4) were found to be isomorphous and of orthorhombic symmetry, forming a complete set of solid solutions. Barium metasilicate, BaO,SiO_2, is not isomorphous with calcium and strontium metasilicates. Felspars analogous to anorthite are formed by both strontium and barium, the latter being monoclinic and forming Carlsbad twins of the contact type.

Measurement of the equilibrium pressure of carbon dioxide in each stage of the reaction in the formation of barium silicate from barium carbonate and silicic acid in the solid state, showed stages with approximate heats of reaction as follows :

$BaO+SiO_2=BaO,SiO_2+26$ kg.-cal. ;
$BaO,SiO_2+BaO=2BaO,SiO_2+21$ kg.-cal. ;
$2BaO,SiO_2+BaO=3BaO,SiO_2+13$ kg.-cal. ;
$3BaO,SiO_2+BaO=4BaO,SiO_2+4$ kg.-cal.

(Grube and Trucksess, Z. anorg. Chem. 1931, **203**, 75) (*v.* PREPARATION OF BARIUM HYDROXIDE).

Barium disilicate, $BaSi_2O_5$, has been prepared synthetically by N. L. Bowen (J. Washington Acad. Sci. 1918, **8**, 265). It crystallises in the orthorhombic system; the terminal angles are 100° and the lateral angles 130°. It is isomorphous with $K_2Si_2O_5$. The colourless six-sided plates which form in optical glass rich in barium have been identified with this compound. Solutions of baryta, when kept in glass bottles for any length of time, deposit transparent rhombic crystals of the composition $BaSiO_3,7H_2O$. These crystals lose their water a little above 100°, and become turquoise-blue : they are decomposed by boiling water, and they may be readily obtained in a few days, by suspending calcined silica in baryta water, when the sides of the vessel become covered with the crystals (Le Chatelier, Compt. rend. 1881, **92**, 931).

Barium aluminates.—Malquori (Gazzetta, 1926, **56**, 51) shows that the following aluminates can be formed by direct union of the two hydroxy hydrates: (1) BaO,Al_2O_3 with 4, 5, and 6 mols. of water, separate *in vacuo* as colourless crystals and are stable in the presence of solutions containing 3·5–2·1% BaO ;

(2) $2BaO,Al_2O_3,5H_2O$;
(3) $3BaO,Al_2O_3(7 \;\&\; 11)H_2O$

stable in presence of solutions with 2·1–1·2% BaO. Each compound is decomposed by excess of water yielding Al_2O_3 and $Ba(OH)_2$. Their use in water purification and for structural clay products has been investigated.

Barium titanate.—When equivalent quantities of titanic anhydride and barium carbonate are fused at a bright red heat for an hour with excess of barium chloride, and the product extracted with very dilute hydrochloric acid, a residue of yellow microscopic crystals resembling cubes and octahedra, of the composition

$$2BaO{\cdot}3TiO_2$$

and of sp.gr. 5·91, remains undissolved These crystals are found on examination by polarised light to consist of aggregations of rhombic lamellæ.

Reactions of the compounds of barium.—When heated on a thin platinum wire in the inner blowpipe flame, or when brought into any non-luminous flame, barium compounds impart a yellowish-green colour to the outer flame. When viewed through the spectroscope two green bands Baα and Baβ come out most intensely ; Baγ, though not so marked, is also a characteristic band. Besides these, there are numerous bands in the red and yellow and one broad indistinct band in the blue, close to Fraunhofer's F. Bunsen found that $\frac{1}{1000}$ of a milligram of barium salt may be detected spectroscopically. Silicates of barium give this reaction on moistening with strong hydrochloric acid (*see* CHEMICAL ANALYSIS).

Estimation of Barium.—*See* CHEMICAL ANALYSIS. G. S. B.

BARKITE. Trade name for di-methyl-*cyclo*hexanyl oxalate,

$$\begin{array}{l} CO{\cdot}OC_6H_{10}Me \\ | \\ CO{\cdot}OC_6H_{10}Me \end{array}$$

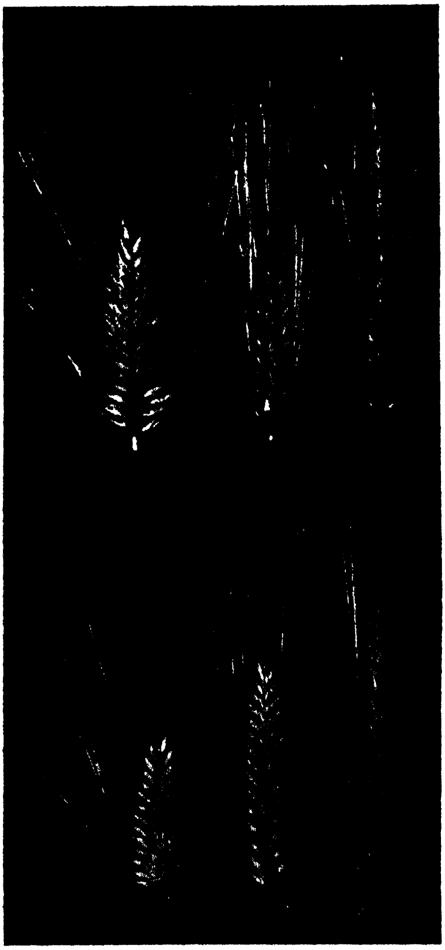
sp.gr. 1·035 ; used in lacquers as a solvent for nitrocellulose and resins.

BARLEY. The term barley refers to a group of closely related sub-species of Graminæ of the genus *Hordeum* and includes many varieties and races. Barley grows wild in south-west Asia and Abyssinia. It has been cultivated from the beginning of civilisation and its main uses have been for food and beer. The associated practices of brewing and baking grew up in the Sumerian Age, some 7,000 years ago, and were passed on from the Euphrates valley *via* Asia Minor to Egypt. Unlike the closely related wheat, barley does not give a coherent gluten; therefore barley dough does not " rise " and is not used in this country for bread-making. The main present-day uses of barley are for stockfeeding, brewing and whisky distilling. Minor uses are as pearl barley, malt extract and barley flour. Pearl barley is barley which has been decorticated by friction, and fairly large grains with a shallow ventral groove are desirable in its fabrication. Malt extract is used in the laundry for destarching purposes, also in pharmacy and, to some extent, in brewing. Small grained, high-nitrogen barley, chiefly from Canada, is employed in its fabrication.

In the barley of commerce, as in wheat, the inflorescence (the ear) consists of a spike with two opposed rows of " fans " alternating up the stalk (rachis). Each fan consists of three spikelets. The main botanical division is (1) fans with all three spikelets fertile—the six-rowed barleys, and (2) those in which only the median one of the three florets of each fan develops—the two-rowed barleys. The intermediate form (*H. intermedium*) is rare; in this the lateral florets are fertile but produce small awnless grains. Each of these main groups is subdivided in the older classifications according to the denseness of the florets on the rachis. The densely crowded ones give short upright spikes (in two-rows—" fan " barleys, *H. zeocriton*, in six-rows—*H. hexastichum*). Then there is the

Six-rowed Barleys.

H. hexastichum. (F. 112.) (Dense.) " Four-rowed." (Chilean.) (Intermediate.) *H. vulgare.* (July.) (Lax.)



" Fan." " Wide " ear. " Narrow " ear.

Two-rowed Barleys.

FIG. 1.

group in which the florets are loosely arranged on the stalk (in the two-rowed Chevallier type—*H. distichum*, in six-rowed—*H. vulgare*). Between the lax and dense types there are intermediate forms (in two-rows—Goldthorpe type—the wide-eared barley of commerce). In certain of the six-rowed barleys the lateral rows from opposite sides overlap, giving an apparent four-rowed barley. The six main types are illustrated in Fig. 1.

Six-rowed barleys can be detected when threshed since two-thirds of the grains (those from the lateral florets) are twisted along their main axis. The dense and lax types can be roughly distinguished by the angle which the point of attachment makes with the grain.

The division on denseness and laxness of the head is convenient in practice, but the occurrence of intermediate forms blurs the distinctions. More recent classifications have been based solely on the sterility or fertility of the florets (H. V. Harlan, Bull. 622 (1918), U.S. Dept. Agric. Bureau of Plant Industry) or the lemma characters (R. G. Wiggans, Cornell Univ. Agric. Expt. Sta. Mem. 46, 1921).

In all classifications there are subdivisions in each group according to whether the glumes adhere to the grain (normal type) or are loose (giving "naked" barley), according to the occurrence or not of pigment in the aleurone layer, according to the occurrence and form of the rachilla. The rachilla is a small bristle lying at the base of the furrow which is present on the ventral side of the grain.

Each grain has a long awn at the apex which is removed in threshing. The structure of the grain is illustrated by a longitudinal section (Fig. 2). In the majority of the cultivated barleys the glumes (paleæ) adhere to the grain forming an outside layer which clasps the ventral palet. Inside comes the kernel consisting successively of pericarp, spermoderm, perisperm, and endosperm. The outer layers of the endosperm consist of the aleurone layer, which in barley is several layers of cells thick and is distinguished in this from other cereals.

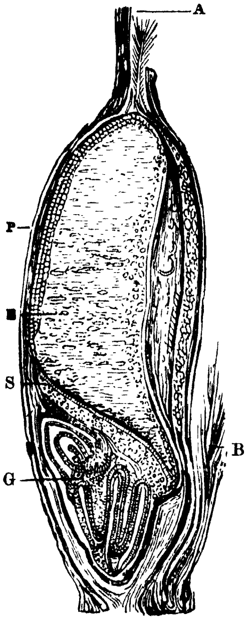
The main interior mass is composed of endosperm, which consists of smaller cells on the outside and larger in the centre. During development carbohydrates and nitrogen compounds pass in, chiefly on the ventral side, and are elaborated.

After fertilisation the nitrogen compounds and carbohydrates pass in, in sensibly constant proportions, so that the nitrogen content of the grain (as a percentage on dry matter) remains fairly constant. It often appears to fall somewhat until 30 grams thousand corn weight is reached and thereafter to rise slightly. It follows that the nitrogen content of immature grain is a rough guide to the content at maturity, and the older idea, that the proteins went in first and the carbohydrates after, is wrong.

The proteins are elaborated almost as soon as the nitrogen enters the grain. The hordein content (*see* below) undergoes little change thereafter, but there is some elaboration of the simpler salt-soluble compounds to glutelin on maturation. The protein regularity described later is the resultant of the regularity in formation during development (L. R. Bishop, J. Inst. Brew. 1930, **36**, 336; G. Hofman-Bang, *ibid.* 1931, **37**, 72).

The scale-shaped embryo lies against the endosperm on the lower dorsal side. The changes which it initiates in germination are dealt with in the malting section of the article on Brewing.

In Great Britain the barley is almost entirely two-rowed and is grown chiefly as a spring crop. Recent hybrid strains have successfully ousted older sorts, at any rate in the south. Among the best are Spratt-Archer, Plumage-Archer, and Golden Archer. In the south-east Plumage-Archer has been successfully grown as an autumn-sown crop (F. C. Hawkes, J. Nat. Inst. Agric. Botany, **2**, 142, 232).



P—palea (husk).
E—endosperm.
S—scutellum.
G—germ.
B—basal bristle.
A—awn.

Fig. 2.

Barley suitable for malting commands a higher price than that for stock-feeding, particularly when of good "quality." The best "quality" fetches twice the price of the worst.

Quality for malting is at present judged on appearance. The characters sought being uniform, plump, large grain of bright yellow colour with a finely wrinkled ("thin") skin, absence of blackened ends or musty smell and with the grain in section appearing "mealy" as opposed to "glassy" or vitreous. "Quality" is usually associated with low nitrogen content, high thousand corn weight, and good germination. Quality for stockfeeding is complementary in that high protein content is desirable.

The main factors determining yield and quality are soil and season, while manuring and variety have subsidiary effects. Medium to light loams which are neutral in reaction (*i.e.* contain sufficient lime) are most consistent in yielding high quality. High rainfall in spring or extreme drought at any period of growth reduces the yield. Most English agricultural soils, except some of the lighter ones, contain sufficient potash and phosphate for barley. On any but a rich soil sulphate of ammonia can be added at the rate of 1 cwt. to the acre. This improves the yield on the average 5 to 6 bushels per acre without detriment to the quality—which is contrary to the older teaching. Early sowing improves the yield and leaving until dead ripe improves the quality (*see* E. J. Russell and L. R. Bishop, J. Inst. Brew. 1933, **39**, 287).

Two-rowed barleys are imported for malting from the Danubian basin, Australia, Chile and Denmark. Six-rowed barleys are imported from California, Chile, Australia, North Africa, the Levant and Canada. The characters vary with the soil and climate of origin and with the variety in cultivation.

CHEMICAL COMPOSITION OF BARLEY.

The *straw* is more variable in composition than the grain. In good ripening seasons, when translocation to the grain has been completed, the straw is poorer in quality. Its composition and quality are affected also by the amount of weeds or of undersown grasses or clover. On the average barley straw has about 14% moisture ; the average composition of the dry straw is :

Cellulose.	Xylan in Cellulose.	Encrusting Hemicellulose.	Lignin.
48–55	11–12	20–30	11–16

Nitrogenous Substances.	Pectin.	Ether Extract.	Ash
2–4	0·5–1·0	1–2	4–7

(Data by courtesy of Dr. A. G. Norman.)

The ash has the following composition (Wolff) :

K_2O	Na_2O	CaO	MgO	Fe_2O_3
23·3	3·5	7·2	2·6	1·1

P_2O_5	SO_3	SiO_2	Cl
4·2	3·9	51·0	3·2

Barley husk, being a vegetative part, is similar in composition to the straw. An approximate analysis is :

Cellulose.	Pentosan.	Pectin.	Lignin
* 32	32	4	18

Nitrogenous Substances.	Ether Extract.	Ash.
3·5	1	8

Barley grain is similar in composition to other cereals and remains fairly constant in composition, although such variations as occur are of considerable importance in brewing. In the harvested state it contains some 10–20% of moisture. On the dry the normal analysis range is :

Starch.	Pentosan.	Cellulose.	Lignin.
* 60–68	8–12	4–5	4

Nitrogenous Substances.	Ether Extract.	Ash.
7–14	2–3	2–3

Sucrose.	Invert.	Pectin.
1·5–2·5	0·1–0·5	0·5–1

The factor taken for calculating nitrogenous substances from nitrogen is the conventional one of 6·25. This is undoubtedly too high and, where possible, doubt should be avoided by giving nitrogen content as such.

The main variation in the composition of barley is naturally in the two main constituents—starch and protein—which of necessity vary inversely with one another.

Carbohydrates.—Starch is the main carbohydrate, it consists of amylose and amylopectin. There is no satisfactory agreement on the relative proportions of these two and according to recent work (D. K. Baird, W. N. Haworth and E. L. Hirst, J.C.S. 1935 1201) the two terms apply to molecules of the same chain length but of differing states of aggregation.

There is a higher proportion of starch in two-rowed varieties than in Californian six-rows, and Bishop and Marx have given evidence that the proportions of the individual carbohydrates are regularly related to the total carbohydrate present and the variety. The practical application of this is that it leads to a method of calculating the " extract " yield of barleys in brewing (L. R. Bishop, J. Inst. Brew. 1936, **42**, 103).

The pentosans consist of urono-xylan, urono-araban (I. A. Preece, J. Inst. Brew. 1931, **37**, 409), and possibly of galactoxylan (Lintner and Düll, Z. angew. Chem. 1891, **4**, 538).

The sucrose occurs mainly in the germ. Its amount appears to vary with the germinative energy (G. Bode, Fort. der Landwirt, 1929, **4**, 545).

In the ungerminated barley the only starch hydrolysing enzyme present is β-amylase. Its true amount can only be estimated after papain digestion.

Nitrogen Compounds.—The nitrogen compounds of barley grain have been shown to consist like those of most other cereals of an albumin (water-soluble), a globulin (salt-soluble), a prolamin, *hordein* (soluble in 70% alcohol), and a glutelin (alkali-soluble), together with amino acids and protein intermediates (T. B. Osborne, J. Amer. Chem. Soc. 1895, **17**, 539).

The amounts of these nitrogen compounds are regularly related to the total nitrogen and the variety (L. R. Bishop, J. Inst. Brew. 1930, **36**, 336). The relation is most accurate when calculated per 1,000 corns, but for simplicity illustrative results are given in Table I on page 648 in the more familiar units of grams of nitrogen per 100 g. dry weight with the corresponding percentages of total nitrogen in brackets.

The composition of some of the individual proteins has been studied by Fischer's ester method and by Van Slyke and related analyses. The ester method shows hordein to be high in proline (13·7%) and dibasic acids (43%). The other individual characteristics are illustrated in Table II on page 648, a table of average values of percentage nitrogen distribution.

References.—H. Lüers and M. Landauer, Biochem. Z. 1922, **133**, 598 ; H. Lüers, Biochem. Z. 1922, **133**, 603 ; E. Takahashi and K. Shirahama, J. Fac. Agric. Hokkaido, 1931, **30**, 119 ;

---

* Somewhat modified from F. Schönfeld, " Brauerei und Mälzerei," I, p. 201, Paul Parey, Berlin, 1930.

TABLE I.—PROTEIN COMPOSITION OF BARLEYS.

Grams of nitrogen per 100 g. dry weight as:

Total Nitrogen.	Salt-Soluble N.	Hordein.	Glutelin.
	Two-row barley, Plumage-Archer.		
1·50	·46 (31%)	·48 (32%)	·56 (37%)
2·00	·52 (26%)	·77 (38%)	·71 (36%)
	Six-row barley, Atlas.		
1·50	·49 (33%)	·39 (26%)	·62 (41%)
2·00	·56 (28%)	·64 (32%)	·80 (40%)
	O.A.C. 21.		
1·50	·44 (29%)	·46 (31%)	·60 (40%)
2·00	·51 (26%)	·70 (35%)	·79 (39%)

TABLE II.

	Albumin.	Hordein.	Glutelin.
Amide N	9–10	23–25	11–16
Humin N	1–2	0·6–1·7	2·5–3
Cystine N	15	0·3–1·6	1·8
Arginine N	11–18	5·0–6·0	11·1
Histidine N	0·2–4·5	1–4	1·8–2·0
Lysine N	8·4–9·7	0·2–1	3·4–5·3
Amino N of filtrate	60·4–58·9	49–54	52–58
Non-amino N of filtrate	2·5–2·7	12–14	7–9

L. R. Bishop, J. Inst. Brew. 1928, **34**, 101; W. F. Hoffmann and R. A. Gortner, Colloid. Sym. Mon. 1925, v, **2**, 209; F. Csonka and D. B. Jones, J. Biol. Chem. 1929, **82**, 17; R. K. Larmour, J. Agri. Res. 1927, **35**, 1091; C. O. Johns and A. J. Finks, J. Biol. Chem. 1919, **38**, 63.

The albumin is a typical plant albumin with an isolectric point at p_H 4·57 (H. Lüers and M. Landauer, Z. Elektrochem. 1922, **28**, 341).

Hordein in its accumulation during development and proportions at different total nitrogen contents shows a close analogy with the corresponding behaviour of starch.

Glutelin is altered in composition by the alkali used in dissolving it and its composition is somewhat uncertain.

Protein dissolving enzymes are present or are formed on germination; they are a protease and peptidase (H. Lundin, Biochem. Z. 1922, **131**, 193; C. K. Mill and K. Linderstrøm-Lang, Compt. rend. Trav. Lab. Carlsberg, 1929, **17**, No. 10; R. H. Hopkins, Biochem. J. 1929, **23**, 1022).

Fats.—K. Täufel and M. Rusch (Biochem. Z. 1929, **209**, 55) give the following values for the composition of barley fat:

Acids %	Characteristics.
Stearic, 2·6	Unsaponifiable 5·4.
Palmitic, 7·4	Saponification number 188·4.
Oleic, 26·5	Iodine number 113·5.
Linolic, 43·7	Rerchert-Meissl number 0·87.
Linolenic, 0·4	Polenske number 0·35.
Total, 80·6	Ester number 159·4.
	Acid number 29·0.

It thus contains a high percentage of unsaturated acids. The total ether extract averages 2·0%.

Phosphorus Compounds.—Values between 0·2 and 0·6% have been reported for lecethin; and 1·2% of phytin ($C_6H_{18}O_{24}P_6$) which occurs chiefly in the husk. Small amounts of nucleic acid occur and free phosphoric acid to the extent of 0·1–0·05%. The enzyme phytase is present.

Mineral Constituents.—Major ash constituents in per cent. on dry grain are:

K_2O	Na_2O	CaO	MgO
0·6–0·9	0·1–0·3	0·07–0·15	0·2
P_2O_5	S	SiO_2	Total Ash
0·8–1·2	0·02	0·5–0·9	3·0

Minor constituents in mg. per 100 g.

Al	Fe	Mn	Cu	Zn
0·7	4–9	12	0·2–0·6	2–3

Other constituents include the enzymes, catalase, peroxidase, and oxidase; vitamins A, B, D, and E, and porphyrin. The presence of tannins in the husk is doubtful. L. R. B.

BARRESWIL'S or FEHLING'S SOLUTION. It has long been known that a mixture of verdegris, honey, and vinegar, when boiled to form an ointment, changes colour from green to red. Vogel (Schweigger's Jahresber. **18**, 162) proved that this was due to the precipitation of cuprous oxide.

Alkaline copper sulphate solution was first used as a qualitative reagent for sugars by Trommer (Annalen, 1841, **39**, 360) and applied to volumetric analysis by Barreswil (J. Pharm.

Chim. 1844 [iii], **6**, 301), who added potassium tartrate to the solution. The method of titration was worked out by Fehling (Annalen, 1849, **72**, 106).

Over fifty formulæ for the solution have been suggested, by Bödeker, Soxhlet, Meissl, Herzfeld, Allihn, Kjeldahl and others (Bruhns, Z. anal. Chem. 1899, **38**, 78). These fall into four groups, employing (1) potassium hydrogen tartrate, (2) potassium sodium tartrate, (3) potassium tartrate, and (4) tartaric acid. Soxhlet's formula is usually preferred, probably on account of its low alkali content: 34·64 g. of pure crystallised copper sulphate are dissolved in distilled water and made up to 500 c.c., and 70 g. of sodium hydroxide (not less than 97%), and 180 g. of Rochelle salt are dissolved in 400 c.c. of distilled water and diluted to 500 c.c. These two solutions are mixed in equal volumes, but it is better to keep them separate until just before use (Z. anal. Chem. 1890, **29**, 615). The mixed solutions must be kept in a tightly stoppered bottle and protected from light (Leighton, J. Physical Chem. 1913, **17**, 205). A test portion should be heated to boiling before use, and rejected if precipitation occurs.

If the alkalinity of the solution is reduced by the addition of mineral acids, reduction occurs, even if the solution is still alkaline to litmus. The reduction may begin in the cold, and is completed by gentle heating. It is attributed to the decomposition of the tartaric acid by the mineral acid (Jovitschitsch, Ber. 1897, **30**, 2431).

Pavy's modification of Fehling's solution consists in adding sufficient ammonia to dissolve the cuprous oxide formed, the proportions recommended being 120 c.c. Fehling's solution, 300 c.c. 0·880 ammonia, 400 c.c. 12% caustic soda, the whole to be made up to 1 litre. This gives a blue liquid, but the solution of cuprous oxide in ammonia is colourless, and the end-point of a titration is therefore indicated by the disappearance of the blue colour. Pavy's solution has two drawbacks: its comparatively low concentration and the ease with which it is oxidised, necessitating exclusion of air during titration.

Müller's solution, which is recommended as being more stable than the mixed Soxhlet solutions (Bruhns, Zentr. Zuckerind. 1932, **40**, 631, 666), contains sodium carbonate instead of sodium hydroxide.

The composition of the salts in Fehling's solution has been investigated by a number of workers. The negative character of its blue ion was first indicated by Kahlenberg (Z. physikal. Chem. 1895, **17**, 586) and confirmed by Küster (Z. Elektrochem. 1897, **4**, 105) and Masson (Phil. Trans. 1899, **192**, 331). Masson electrolysed a solution, as free as possible from alkali, in conjunction with a solution of copper sulphate, the blue ions of the two solutions travelling in opposite directions along a tube containing a jelly solution of potassium chloride. The presence of an invisible ion, probably tartaric ion, accompanying the negative blue ions, was demonstrated by the formation of a precipitate at the boundary of the positive blue ions when the negative ions were still some way off.

Masson and Steele (J.C.S. 1899, **75**, 725) isolated and analysed a blue salt thought to be formed from cupric tartrate according to the equation:

$$5NaOH+4CuC_4H_4O_6 = Na_2C_4H_4O_6+Na_3C_{12}H_7Cu_4O_{18}+5H_2O$$

and to combine with the excess alkali in the solution.

The composition of Fehling's solution not being constant, it is not surprising that a variety of copper compounds have been detected in it. Among these are:

$$C_8H_4O_{12}CuNa_2K_2,$$
$$C_8H_4O_{12}CuNa_3K,$$
$$3CuC_4H_4O_6{\cdot}5Cu(OH)_2$$

(Morton, Quart. J. Pharm. 1931, **4**, 161); the basic salt $Cu(OH)_2{\cdot}CuT$ exists only when comparatively little alkali is present, and other basic salts such as $CuT{\cdot}5Cu(OH)_2$ are present as colloids ($T=C_4H_4O_6$ or $C_4H_2O_6$). Positive or negative sols can be obtained by varying the composition of the solution (Dumanski and Dikanova, J. Gen. Chem. Russ. 1931, **1**, 163; A. 1931, 907; 1932, 692). These colloids are thought to account for the formation of copper oxide sols, ageing phenomena and consequent difficulties which arise in sugar estimation (Dumanski and Chalisew, Kolloid-Z. 1929, **47**, 121; Chem. Zentr. 1929, II, 1546).

The importance of Fehling's solution is due to its ready reduction by a number of substances, particularly the aldehyde sugars. It is *not reduced* by cane sugar, dextrin, or cellulose, but *is reduced* by dextrose, laevulose, maltose, lactose, mannose, galactose, arabinose, gallisin, aldehydes generally, chloral, chloroform, resorcinol, pyrogallol, gallotannic and trichloracetic acids, arsenic, antimony and bismuth (Kohn, Monatsh. 1921, **42**, 83). The mechanism of the reduction is doubtful. Among the products are formic, acetic and tartronic acids, some acids of doubtful composition and a gum-like substance.

Any of the above-mentioned reducing compounds may be detected by heating the clear, acid-free liquid with twice its volume of Fehling's solution, when cuprous oxide is precipitated. The precipitate is at first yellow but changes to orange-red or bright red, the colour depending on the conditions of precipitation and the difference being due to differences in particle size (Fischer and Hooker, J. Lab. and Clin. Med. 1918, **3**, 6). If the liquid to be tested is much coloured, it must first be clarified as described under SUGAR ANALYSIS.

Fehling's solution is chiefly used for the estimation of the reducing sugars, either gravimetrically or volumetrically; cane sugar and starch may be estimated by the same methods if they are first converted into invert sugar by heating with hydrochloric acid and afterwards neutralising with sodium carbonate. In all these estimations the maintenance of constant conditions, temperature, tartaric acid content, etc., is of the greatest importance. It is immaterial whether *d*- or meso-tartaric acid is used (Sobotka, J. Amer. Chem. Soc. 1933, **55**, 2164). Lane and Eynon (J.S.C.I. 1925,

44, T, 150) point out that error may arise from the varying copper content of $CuSO_4{\cdot}5H_2O$ due to variation in moisture. This and other errors can be eliminated by standardisation shortly before use against invert sugar (Case and Price, J. Inst. Brew. 1933, **39**, **36** ; B. 1933, 203) or against pure glucose. The latter has the advantage that the strength of the glucose solution can be checked by means of the polarimeter (Main, Internat. Sugar J. 1933, **35**, 43 ; B. 1933, 326). According to Bruhns (Zentr. Zuckerind. 1922, **30**, 1473), solid impurities act as boiling stones, lowering the boiling temperature and causing incomplete precipitation. It is therefore desirable either to remove these impurities by filtration or to ensure uniform conditions by adding talcum powder.

Various indicators have been proposed to facilitate titration with Fehling's solution. Potassium ferrocyanide can be used as an external indicator if a portion of the solution is filtered off, but this procedure is inaccurate and tedious. Ferrous thiocyanate is a more satisfactory indicator for cupric ion. Starch and potassium iodide, acidified with acetic acid, give a blue colour when the Fehling's solution is in excess, owing to the liberation of iodine by the cupric ion. According to Bruhns (Zentr. Zuckerind. 1932, **40**, 631), the latter two methods are untrustworthy unless the solution is cooled below 20°. The best indicator is methylene blue, which can be used internally, even in cloudy solutions. It is reduced to its leuco base by the slightest excess of aldose or ketose, the colour being restored by a trace of cupric salt (Lane and Eynon, J.S.C.I. 1923, **42**, T, 32). This method has been adapted to the determination of sugar in urine (Lane and Eynon, Analyst, 1924, **49**, 366). The end-point can also be determined electrometrically.

BARUTIN. Trade name for the double salt of theobromine barium and sodium salicylate.

BARWOOD. Barwood is the wood of the *Baphia nitida* (Lodd.), imported from the west coast of Africa, *e.g.* Sierra Leone, Angola, etc. Its physical properties are very similar to those of sanderswood, but in the rasped condition it has a brighter red colour and is devoid of aromatic odour. According to Girardin and Preisser, boiling water extracts about 7% of colouring matter, alcohol 23%, and ether 10%.

Anderson (J.C.S. 1876, ii, 582) isolated a number of substances from barwood and described the following :

Baphiin, $C_{24}H_{20}O_8$, m.p. about 200°, lustrous tabular crystals (from alcohol), has an odour of orris root, and is insoluble in water and sparingly so in benzene. The alcoholic solution on exposure to air yields orange-red or pale purple colours.

Baphic acid, $C_{24}H_{22}O_9$ or $C_{24}H_{22}O_{10}$, white nacreous scales, prepared from baphiin with hot dilute caustic potash, is readily soluble in ether, less so in alcohol (*cf.* Santal, below).

On boiling baphiin with a strong aqueous solution of caustic potash without access of air, three substances are produced : (1) *baphinitin*, moderately soluble in alcohol or ether ; (2) *baphinitone*, very soluble in these liquids ; and (3) a trace of a substance, granular crystals, m.p. 164·1°, very sparingly soluble even in hot alcohol.

Baphinitin, $C_{24}H_{24}O_6$, white needles soluble in alcohol, but insoluble in water, has the same odour as baphiin but stronger, and is probably identical with pterocarpin (*cf.* SANDERSWOOD).

Baphinitone, white lustrous crystals, m.p. about 88°, $C_{26}H_{26}O_6$ (Anderson), forms a *tribromo*-derivative, $C_{26}H_{23}Br_3O_6$, melting at 180·2°. Baphinitone, according to Ryan and Fitzgerald (Proc. Roy. Irish Acad. 1913, **5**, 106), is homopterocarpin, $C_{17}H_{16}O_4$, which has m.p. 84° and is identical with that existing in sanderswood.

In addition to these substances, Anderson describes at least three colouring matters. These are insoluble in benzene and give purple lakes with lead acetate and purple solutions with alkalis.

O'Neill and Perkin (J.C.S. 1918, **113**, 125), employing methods they had previously applied to sanderswood, obtained a chocolate-red colouring matter in the form of a powder possessing the formula $C_{22}H_{16}O_5(OMe)_2$, decomposing at about 270°. Its colour reactions are similar to those described for the santalin of sanderswood, and there is little doubt that the two compounds are identical.

After removing santalin, these authors isolated a compound resembling *deoxysantalin* (*cf.* sanderswood), the true colouring matter, and, in addition, two crystalline substances identical with those previously described by Weidel (Zeitsch. für Chem. 1870, **6**, 83). *Santal* (*a*), flat needles or plates, m.p. 222°–223°, sparingly soluble in absolute alcohol, has the formula $C_{15}H_9O_5(OMe)$, and not $C_8H_6O_3$, as proposed by Weidel. Santal, which seems to correspond with Anderson's baphic acid, is readily soluble in dilute alkali hydroxides, and by the action of hydriodic acid is converted into *santol*, probably $C_{15}H_{10}O_6$, small colourless flat needles, m.p. 270°–273°. Its colourless solution in dilute alkali hydroxide soon develops a reddish violet tint, and then, on acidification, deposits yellow crystals. If the mixture is now boiled, these become colourless, apparently with regeneration of santol, which thus appears to contain a lactone group.

The second substance (*b*), termed by O'Neill and Perkin *santalone*, is evidently Weidel's substance $C_{14}H_{12}O_4$. This is sparingly soluble and crystallises from alcohol in small red leaflets. It is soluble in dilute alkalis with a red colour, whereas alcoholic ferric chloride colours it a violet tint, and it appeared to darken at about 280°, melting at 300°. O'Neill and Perkin suggest its formula as either $C_{22}H_{13}O_4(OMe)_3$ or $C_{22}H_{15}O_4(OMe)_3$, corresponding to that of a *deoxysantalin monomethyl ether* with which its general properties harmonise.

A. G. P. and E. J. C.

BARYLITE. This mineral was first described from Långban, Sweden, by C. W. Blomstrand in 1876, as a barium aluminium silicate. It has been shown since to have the composition $Be_2BaSi_2O_7$ (G. Aminoff, Geol. För. Förh. Stockholm, 1923, **45**, 124) ; and this is confirmed by the subsequent discovery of the same mineral at Franklin Furnace, New Jersey (C. Palache and L. H. Bauer, Amer. Min. 1930, 15, 29). It forms colourless orthorhombic plates, sp.gr. 4·027, 4·066 ; and its presence in the Franklin Furnace ores was first detected by the vivid blue fluorescence that it shows in ultra-violet rays. L. J. S.

BARYTA GREEN *v.* Barium.

BARYTE. Barite, barytes, or heavy-spar (from *βαρύς*, heavy) ; a common mineral consisting of barium sulphate ($BaSO_4$), and crystallising in the orthorhombic system. The name barytes is, however, sometimes loosely, but incorrectly, applied to include both this species and the mineral witherite ($BaCO_3$, *q.v.*), or these are occasionally referred to as "sulphate of barytes" and "carbonate of barytes" respectively. The reason for this confusion is that the two minerals are often mined together, although they are not always put to the same uses.

Baryte is frequently to be found as well-developed crystals, which vary considerably in their appearance and habit. They possess a perfect cleavage parallel to the base, and perpendicular to this are two prismatic cleavages parallel to the faces of the primitive rhombic prism, and inclined to one another at an angle of 78° 22½′. With these three directions of perfect cleavage, massive baryte sometimes presents a certain resemblance to calcite, and its hardness is also about the same (H=3). The angles between the cleavages are, however, different ; and, further, baryte may be readily distinguished from calcite by its heaviness (sp.gr. 4·5), and from both calcite and witherite by not effervescing with acid. The massive material is often white and opaque ; but crystals are sometimes transparent and colourless, or with brownish, greenish, or bluish shades of colour.

Baryte is usually met with in veins, often in association with ores of lead. Some of the old lead mines of the north of England, Derbyshire and Shropshire are now being reworked for baryte. A remarkable vein of baryte, consisting of pure white massive material with a thickness varying from a few inches to 16 feet, was formerly extensively worked in the coal-measures at New Brancepeth Colliery, near Durham (L. J. Spencer, Min. Mag. 1910, 15, 302). Beautiful crystallised specimens are abundant in the hæmatite mines of west Cumberland, but, owing to the brown or yellow colour of this material, it is of no commercial value. A pure white granular baryte resembling marble in appearance is mined at Dunmanus Bay in Co. Cork ; and deposits have been worked at several places in Scotland. Important deposits of the mineral are worked in the United States, Germany, Rhodesia, etc. Baryte occurs abundantly as a cementing material in Triassic sandstones in the Midlands of England (F. Clowes, 1889, 1899) ; and it has been suggested that this could be easily won by washing.

Baryte is mainly used in the manufacture of paints, not only of white paint, but as an inert body in coloured paints. Lithopone paint consists largely of barium sulphate with zinc oxide and sulphide. It is often suggested that baryte is used for adulterating various articles. Barium sulphide and carbonate are also prepared from baryte by roasting it with coal, and from the product barium chloride, barium hydroxide, etc., are prepared. In preparing the crude baryte for the market, it is coarsely crushed and hand-picked ; or when mixed with rock and dirt, these are separated by agitation (jigging) in water. Coloured impurities are sometimes extracted by steam-boiling with sulphuric acid. The purified material is kiln-dried and reduced to very fine white powder in a ball-mill provided with screens, or between millstones. The barytes flour so prepared still consists of minute crystalline (cleavage) particles, and it is this that gives the "tooth" or adhesive properties to the coarser barytes paints. The finer qualities ("blanc fixe") are prepared from precipitated barium sulphate ; and this is also used for dressing cloth and leather, and for producing the smooth coating on "art" papers.

References.—Barium minerals, Imperial Institute (Mineral Resources), London, 1921. For details of British occurrences, *see* "Special Reports on the Mineral Resources of Great Britain," vol. ii, Barytes and Witherite, Mem. Geol. Survey, 2nd ed. 1916. A list of all known localities in the north of England and Derbyshire with maps is given by J. M. Sweet, Min. Mag. 1930, 22, 257. For the United States, and a general account with bibliography, *see* "Mineral Resources of the United States," for 1915, U.S. Geol. Survey, 1916 ; H. Ries, "Economic Geology," 6th ed., New York, 1930. L. J. S.

BARYTIC WHITE or PERMANENT WHITE or BLANC FIXE *v.* Barium ; also Pigments.

BARYTO-CELESTITE *v.* Barium.

BARYTOCALCITE. Barium and calcium carbonate, $BaCO_3 \cdot CaCO_3$, crystallising as prismatic and blade-shaped crystals in the monoclinic system. There are good cleavages in three directions (the basal plane and a prism), and curiously the angles between these are near to the angles between the three cleavages of calcite. The composition is the same as that of alstonite (*q.v.*), but whilst alstonite is an isomorphous mixture of barium and calcium carbonates, barytocalcite is a double salt. The mineral is white or colourless, and has a vitreous lustre. Sp.gr. 3·65 ; hardness 4. Apart from a doubtful record from Glamorganshire, the mineral has been found only in the old Blagill, or Bleagill,[1] and Ayle Burn lead mines, near Alston in Cumberland, and along the same vein into West Allendale in Northumberland, where it occurs in considerable quantity and was at one time mined as a "low-grade witherite" ($BaCO_3$ 66·3%). Large blocks of massive material with crystal-lined cavities may still be found lying outside these abandoned mines.

L. J. S.

BASALT. A group of volcanic rocks of basic composition (SiO_2 45–55%), corresponding with the plutonic gabbros. The name is one of the oldest in petrography, being of Ethiopian origin and said to signify a stone that yields iron. Many of the ancient Egyptian and Assyrian monuments were carved in basalt, and it is the material of the famous Rosetta stone. The term is used in rather different senses. A quarryman often recognises amongst the difficultly worked igneous rocks only granite and basalt, and commonly any dark-coloured fine-grained rock is included under the term basalt or trap-rock. Also petrographers are not agreed amongst themselves as to the limitations of the term. Strictly, it should be applied to a rock which has flowed as a lava on the earth's surface, and is composed of a basic plagioclase-felspar (bytownite or labradorite) and augite, together with small amounts of magnetite and ilmenite, and sometimes glassy (uncrystallised) material in the ground-mass. Sometimes porphyritic crystals are present, but usually the component minerals can only be recognised when thin sections of the rock are examined under the microscope ; the rock appearing compact and homogeneous to the unaided eye. Other minerals are sometimes present, particularly olivine, and we then have the varieties olivine-basalt, hornblende-basalt, etc. In a less common type of alkali-basalt the felspars are partly or wholly replaced by felspathoid minerals (nepheline, leucite, and melilite). When the felspars are wholly replaced we have the varieties nepheline-basalt, leucite-basalt, etc. ; and when both felspar and felspathoid are present the rock is termed tephrite or basanite, according as olivine is absent or present. A leucite-basanite, then, consists of plagioclase, augite, olivine, and leucite. Analyses of some of these types of basaltic rocks are given below : I, average of 198 analyses of typical basalts, including olivine-basalts ; II, basalt from Disko Island, west Greenland ; III, olivine-basalt from the Isle of Skye, Scotland ; IV, leucite-tephrite from Rome ; V, leucite-basalt from Highwood Mountains, Montana.

---

[1] A corruption of the German blei (lead), and a relic of the German miners employed in the Cumberland mines in the reign of Queen Elizabeth.

	I.	II.	III.	IV.	V.
SiO_2 . .	49·06	47·11	46·61	50·25	47·98
TiO_2 . .	1·36	0·78	1·81	0·57	0·58
Al_2O_3 . .	15·70	14·33	15·22	21·41	13·34
Fe_2O_3 . .	5·38	4·88	3·49	1·76	4·09
FeO . .	6·37	11·06	7·71	1·82	4·24
MnO . .	0·31	0·21	0·13	—	trace
CaO . .	8·95	9·12	10·08	4·48	9·32
MgO . .	6·17	8·45	8·66	0·31	7·01
Na_2O . .	3·11	1·91	2·43	5·16	3·51
K_2O . .	1·52	0·20	0·67	11·32	5·00
H_2O . .	1·62	1·52	3·17	0·96	2·10
P_2O_5 . .	0·45	0·29	0·10	0·12	1·03

As a consequence of their volcanic origin, basalts often exhibit a vesicular texture, owing to the expansion of water-vapour in the rock before consolidation ; and in these cavities secondary minerals (chalcedony, calcite and zeolites) are often deposited. A well-marked columnar structure, often on a large scale, is a common character ; *e.g.* at the Giants' Causeway in Co. Antrim, the Staffa caves in the Western Isles of Scotland and in the Linz basalt quarry on the Rhine. It is a dense black rock weathering to brown or dark green. Sp.gr. 2·8–3·1. The crushing strength is high (2,000–3,000 tons per square foot) ; the absorption for water low (about 1%) ; and the conductivity for heat considerable, buildings of basalt being for this reason cold in winter and hot in summer.

Basalts are of world-wide distribution, and sometimes cover enormous tracts of country ; *e.g.* the Arctic region extending to the Western Isles of Scotland, and the north of Ireland, the Deccan traps of India, and the lava-fields of Washington, Oregon, and Idaho. The rock is quarried at many places for road-metal and paving stones, and on the Continent as a building stone. But it is to be remembered that much of the rock quarried under the name of basalt is included by petrographers under other terms, particularly dolerite and diabase (*q.v.*). The types of alkali-basalts are less widely distributed, but are abundant in central Italy, in the neighbourhood of Rome and Vesuvius, and are known in Germany, Bohemia, Wyoming, Montana and Brazil. These are of importance on account of their high content of potash (analyses IV and V above). L. J. S.

BASANITE *v.* Basalt.

BASIL, ESSENTIAL OIL OF. The oil distilled from the fresh herb *Ocimum basilicum*, N.O. Labiatæ, the sweet basil, of which there are several varieties. It is produced in France, Germany, Spain and Algeria. The yield is about 0·1% from the *crispum* variety.

Characters : sp.gr. 0·904 to 0·930, but figures up to 0·987 have been recorded ; opt. rot. −6° to −22°, but dextro-rotatory oils have been obtained in Réunion ; n_D^{20} 1·481–1·517. Soluble in 3 volumes of 80% alcohol.

It contains methyl chavicol, eugenol, *l*-linalol, cineole, *d*-*a*-pinene, *d*-camphor and an olefinic terpene, ocimene. Up to 55% of methyl chavicol has been found by E. G. and E. Camus (Roure-Bertrand Fils, Bull., Oct. 1910, p. 23).

Oils from other species of *Ocimum* have been examined, notably that from *Ocimum canum*, which contains about 80% of methyl cinnamate, and that from *Ocimum viride*, which contains about 30% of thymol.

An interesting article on the production of basil oils in the Seychelles is to be found in the Bulletin of the Imperial Institute, 1934, Vol. XXXII, No. 4. C. T. B.

BASLE BLUE *v.* Azines.

BASSIA FATS. Under this name are comprised a number of similar fats derived from the seeds of Indian or African trees of the genus *Bassia* (Koenig)[1] and related genera of the Natural Order *Sapotaceæ*, of which Mowrah (Mahua) Butter, Illipé Butter, Phulwara Butter, and Shea Butter are the most important.

---

[1] As the generic name *Bassia* is familiar to technologists through long usage, it has been retained for the various trees concerned in the present article, although strictly such nomenclature may no longer stand, for Macbride (Contrib. Gray Herb. n.s. liii, 17, 18 (1918)) has pointed out that the use of the name *Bassia* by Allioni in 1766 for a genus of the N.O. *Chenopodiaceæ* antedates and invalidates its application by Koenig (1771) to plants of the Order *Sapotaceæ*. Accordingly, the name *Bassia* (Koenig) has been replaced by *Madhuca* (Gmelin), and the trees referred to above as *Bassia latifolia*, *B. longifolia*, and *B. butyracea* should correctly be cited as *Madhuca latifolia* (Roxb.) Macbride, *M. longifolia* (L.) Macbride, and *M. butyracea* (Roxb.) Macbride.

Mowrah (Mahua) Butter (Bassia Tallow) is, properly, the fat obtained from the seeds of *Bassia latifolia*, Roxb. (*Madhuca latifolia* (Roxb.) Macbride=*Illipé latifolia* (Roxb.) Engler=*B. villosa* Wall.), a tree which is widely distributed in the Northern and Central provinces of India, especially in Bengal, and is frequently cultivated in small plantations in Eastern India. It is generally known in India under the Hindustani names of "Mahua," "Mohua," "Mahwa," or "Mowha," but in some districts the Tamil names "Illipi" or "Illupei" are used. Unfortunately, the same native names are also applied to *B. longifolia* L., but, since the latter species occurs only in Southern India, it is more commonly called by the Tamil names: in the older literature, however, as well as in many modern German memoirs, the fat of *B. longifolia* is commonly referred to as "Mowrah fat" (*cf.* Crossley and Le Sueur, J.S.C.I. 1898, **17**, 991; Moore, Young, and Sowton, Biochem. J. 1910, **5**, 94).

The kernels of *B. latifolia*, which contain about 45–50% of fat, are from 1–2 cm. long and are enclosed in a light brown, shiny husk; although somewhat smaller, the seeds closely resemble those of *B. longifolia*, with which they are frequently confounded.[1] Similarly, the fats obtained from the two species are often confused, which is partly due to the fact that the two kinds of fat are often mixed together when exported to Europe, a practice which is assisted by the duplication of the native names for the two species.[2]

In its fresh state, mowrah fat is yellow, but it can be bleached by exposure to the air or by chemical methods.

The fat has a buttery consistency and a bitter aromatic taste and a peculiar odour, which need not be unpleasant, however, if the seeds have been properly collected and stored: it has d_{15}^{15} 0·917, m.p. 25°–30°C., and solidifies at 18°–22°C. The iodine value usually lies between 54 and 63, but extremes of 52·6 and 67·9 have been recorded (*cf.* Crossley and Le Sueur, J.S.C.I. 1898, **17**, 989; Bull. Imp. Inst. 1913, **11**, 559). About 1–2·5% of unsaponifiable matter is present.[3]

Dhingra, Seth, and Speers (J.S.C.I. 1933, **52**, 116T) report the following composition for the fatty acids derived from a specimen of mowha fat having an iodine value of 55·8: myristic acid, 1%; palmitic acid, 16·0%; stearic acid, 25·1% (*cf.* Menon, J.S.C.I. 1910, **29**, 1428); arachidic acid, 3·3%; oleic acid, 45·2%; linolic acid, 9·4%.

Mowrah seeds and fat are fairly important articles of commerce: the expressed fat is used in Europe and in India as a raw material for soap and candle manufacture; it is also used in India for edible purposes, particularly as a substitute or adulterant for tallow and ghee, and as a medicinal oil in the treatment of skin diseases. As the crude fat may possibly contain traces of toxic saponins, it should be properly refined before use as a foodstuff. The expressed mowrah seed-cake is used as a manure; owing to its bitter taste and the presence of poisonous saponins, it is unsuitable for the feeding of cattle (*cf.* Illipé Butter, below). Nevertheless, the cake has frequently been added as an adulterant to the so-called "native linseed cake," which, under this misleading name, has at times found extensive sales on the Continent.

Illipé Butter (also known in Ceylon as **Mee Oil**; occasionally erroneously referred to as Mowrah butter, *q.v.* above) is the fat obtained from the seeds ("illipé nuts")[1] of *Bassia longifolia* L. (*Madhuca longifolia* (L.) Macbride=*Illipé malabrorum* Kön.), a tree indigenous to Southern India and Ceylon, where it replaces the *B. latifolia* (Mowrah, Mahua) of Northern India. (A variety of *B. longifolia*, known as *B. malabarica* Bedd. (the "att-illupei") is found in the Western Ghats.) Illipé seeds are similar to those of *B. latifolia*, but are mostly longer (3–4 cm. in length) and less rounded; the kernels, which constitute 75% of the seed, contain 50–55% of a white, or pale yellow, soft fat, which closely resembles mowrah butter, but has slightly lower melting and setting points. Correspondingly, the iodine value is slightly higher than that of mowrah fat, being usually about 60. The fatty acids contain stearic acid (12–20%, Menon, J.S.C.I. 1910, **29**, 1428), a considerable proportion of palmitic acid (*cf.* Winterstein, Z. physiol. Chem. 1919, **105**, 31), oleic acid and linolic acid (about 51% and 9% respectively: R. G. Pelly, J.S.C.I. 1912, **31**, 98, *cf.* Bull. Imp. Inst. 1911, **9**, 231). An unsaturated hydrocarbon *illipene* was isolated from commercial illipé butter ("probably a Bassia fat") by Kobayashi (J.S.C.I. Japan, 1922, **25**, 50B, *cf.* Bauer, Chem. Umschau, 1923, **30**, 97) to which the formula $C_{64}H_{106}$ or $C_{65}H_{108}$ has been attributed by Tsujimoto (J.S.C.I. Japan, 1929, **32**, 365B), and which is probably identical with the hydrocarbon "karitene" present in shea fat (*see* below).

Kobayashi also reported the presence of four alcohols of high molecular weight in that part of the unsaponifiable matter from illipé fat which was not precipitated by digitonin, whilst Tsujimoto characterised a sterol, termed *bassisterol*, m.p. 210°–211°, which is probably identical with *lupeol* (*cf.* occurrence of *lupeol* in shea fat).

Illipé butter is used for the same purposes as mowrah fat (*q.v.*). Similarly, the expressed seed-cake contains toxic glucosides, and is only used as manure, or as an unguent by the natives of India. (In Ceylon, the cake or poonac is exported under the name "arappo.") The saponin from the cake of *B. longifolia* has been studied in detail by B. Moore, Baker-Young and Sowton (Biochem. J. 1910, **5**, 94) and by Spiegel and Meyer (Ber. deut. pharm. Ges. 1918, **28**, 100); the name "mowrin" (German "Movrin") used by these authors for the saponin is a misnomer, as they appear to have been dealing with *B. longifolia* cake.

---

[1] It may be noted that H. J. Lam, the author of the most recent taxonomic work on the *Sapotaceæ*, regards *Madhuca* (*Bassia*) *latifolia* as identical with *Madhuca* (*Bassia*) *longifolia*.

[2] The suggestion of Bolton and Revis ("Fatty Foods," 1913, p. 183) to prevent confusion by using the names "Latifolia fat" and "Longifolia fat" for the products of the respective species has not been generally adopted.

[3] The unsaponifiable matter in *Bassia* fats contains highly unsaturated substances (*see* Shea fat, Phulwara butter); consequently the iodine value of the separated fatty acids freed from unsaponifiable matter is usually a few units lower than the iodine value of the fat.

[1] These Indian "illipé nuts" must not be confused with Borneo (Pontianak, Sarawak, Siak) illipé nuts derived from species of *Shorea* and *Palaquium* (*v.* BORNEO TALLOW). The proposal to employ illipé fat as a chocolate fat appears to be due to such confusion between the Indian and the (miscalled) Borneo illipé seeds.

Phulwara Butter is the fat obtained from the kernels of *Bassia* (*Illipé*) *butyracea* Roxb. (=*Madhuca butyracea* (Roxb.) *Macbride*= *Diploknema butyracea* (Roxb.) Lam), the "Indian butter tree" ("phulwara," "churi," "yel"; the fat itself is termed "phulwa"), which flourishes in the United Provinces and in the Sub-Himalayan tracts of India. The seeds are smaller and thinner than those of *B. latifolia.* The kernels (about 70% of the seed) contain from 60–70% of the pale, hard fat, which is slightly stiffer than lard or ghee and possesses an agreeable odour and taste. It is extensively used in India for edible purposes, either alone or as an adulterant of ghee, and is also valued as an unguent. The fat melts at about 41°–43°C. (Diedrichs, Z. Unters. Nahr. Genussm. 1914, **27**, 135; *cf.* m.p. 39°–51°C. according to Menon, J.S.C.I. 1910, **29**, 1428), and has an iodine value between 42 and 50. From 2–5% of unsaponifiable matter (having an iodine value of about 77) is present. The fatty acids consist almost entirely of palmitic acid (*ca.* 56%) and oleic acid; stearic acid appears to be absent (Menon, *l.c.*), and only very small amounts of acids more unsaturated than oleic acid can be present (Pelly, J.S.C.I. 1912, **31**, 98). Phulwara butter is frequently adulterated with mowrah fat or kokum butter (from *Garcinia purpurea* Roxb.). The residual oil-cake from phulwara seeds contains a saponin (Diedrichs, *l.c.*).

Shea Butter (Karité Butter) is the fat obtained from the seed-kernels of *Butyrospermum Parkii* (G. Don) Kotschy (syn. *Bassia Parkii* G. Don), a tree which grows in enormous quantities in West Africa and through Central Africa in the French and English Sudan, being particularly abundant in the middle basin of the Niger. The tree was first described by Mungo Park, who found it in the kingdom of Bambara, whence the fat was known as Bambara- or Bambooi-fat; other current names are Galam-, Bambuk-, or Lulu-butter (in the Sudan) and, in the French colonies, *Karité* butter (oil).

The shea "nut" (strictly speaking, the seed) is ovoid in shape and about an inch long; it consists of 30–40% of a thin brittle shell (which is easily detached and is removed before exporting the kernels) and 60–73% of kernel. Owing, possibly, to the wide distribution of the tree, specimens of the nuts from different sources show characteristic minor differences in shape, size, fat-content, etc. A special variety appears to be represented by the tree known as *B. niloticum* (Kotschy and Chev) (*cf.* Bull. Imp. Inst. 1908, **6**, 449).

The proportion of fat in the kernels varies within wide limits, *viz.* 30–57% (usually about 50%) according to the origin and ripeness of the seeds. The crude fat, as prepared formerly for export by the African natives by boiling out the pounded kernels with water, had a grey or greyish-white colour and was characterised by a strong indiarubber-like odour and taste. A better grade of white fat, which is prepared by the natives for their own use in a more careful manner, is extensively used as an edible fat and also for burning and cosmetic purposes. The bulk of the exported shea products consists, however, of the shelled kernels, as with the methods of expression available in Europe white or pale yellow fats with a less pronounced flavour can be obtained. (The fat expressed in this country from imported nuts is known as "shea nut oil.")

Crude shea butter contains considerable amounts of caoutchouc-like unsaponifiable substances (*see* below), which have hindered any extensive use of the fat for soap-manufacture; but methods for removing part of the unsaponifiable matter have been devised. Since, however, modern processes of refining and deodorising have made it possible to produce a colourless, odourless shea fat, the most important use of refined shea fat in Europe is for edible purposes, as a chocolate fat and, especially, as an ingredient of lard substitutes (frying fats).

Exports of shea nut products (chiefly kernels) from Nigeria totalled about 9,300 and 7,450 tons (respective values £106,600 and £46,300) in 1928 and 1931 respectively.

Shea fat melts at about 23°–25°C. From 3–9% of unsaponifiable matter is normally present in the crude fat, but the amount may run as high as 12%, and occasionally even up to 16%, especially in fats from immature nuts (*cf.* Bull. Imp. Inst. 1930, **28**, 123; *ibid.* 1931, **29**, 407; 1933, **31**, 334; 1936, **34**, 437).

According to the amount of unsaponifiable matter present, the saponification value of shea fat varies normally from 177–185 (extremes of 172 and 196 have been recorded); similarly the iodine value varies from 56 to 69.

Lewkowitsch ("Oils, Fats, and Waxes," 6th ed., vol. II, p. 537) found from 33·7 to 37·3% of stearic acid (by direct determination) in a number of shea fats examined, which is in agreement with the most recent and detailed examination of a sample of refined shea fat (iodine value 57·3, unsaponifiable matter 9·5%) by Hilditch and Saletore (J.S.C.I. 1931, **50**, 470) who find the following composition for the fatty acids (freed from unsaponifiable matter): stearic acid, 35·9%; palmitic acid, 8·5%; oleic acid, 49·9%; linolic acid, 5·3%. Palmitic acid was also found in shea fatty acids by Hebert (Mat. Grasses, 1911, 2170) but could not be identified in a sample examined by Ehrenstein (Chem.-Ztg. 1925, **49**, 799). The "unsaponifiable matter" from shea butter contains an unsaturated caoutchouc-like hydrocarbon, *karitene*, m.p. 63°–64° ($C_{30}H_{52}$, $C_{32}H_{56}$ or $(C_5H_8)_{20-21}$?), which is probably identical with *illipene* from illipé butter (*q.v.*)[1] (Hopkins and Young, J.S.C.I. 1931, **50**, 389T; Bauer and Umbach, Ber. 1932, **65**, 859; Heilbron, Moffet, and Spring, J.C.S. 1934, 1583). Ehrenstein

---

[1] It may be noted that the shea tree, like most other trees of the *Sapotaceæ* family, yields a gutta-percha-like latex ("karité-caoutchouc").

(*l.c.*) reports the presence of a polymerisable substance (? karitene) and a sterol, m.p. 149°C., whilst Heilbron, Moffet, and Spring (*l.c.*) have identified β-amyrin, m.p. 193°–194°C., lupeol, m.p. 210°–211°C. and an alcohol (sterol ?), m.p. 141°C., in addition to karitene.

Less important Bassia Fats.—Fats closely resembling shea fat are obtained from the seeds of allied African species of the family *Sapotaceæ*, such as the **Djavé** or **Ouréré**, *Bailonella toxisperma*, Pierre and Dubard (syn. *Bassia Djavé*, De Lanessan ; *Mimusops Djavé* (De Lanessan) Engler; *Bassia toxisperma* Raoul) of West Africa, Gaboon, and the Cameroons (*cf.* Perrot, Bull. Sci. Pharm. 1914, **21**, 173 ; Bolton and Hewer, Analyst, 1922, **47**, 282 ; Margaillan, Ann. Mus. Col. Marseille, 1925, **33**, iv (3), fasc. 2, 10), the **Noumgou**, *Dumoria africana* Chev. (syn. *Tieghemella africana*, Pierre) (*cf.* Pieraerts, Adriaens and Meulenberg, Mat. Grasses, 1929, 8701 ; 1930, 8726 *et seq.*, and the **Baco** or **Abaku**, *Dumoria Heckeli* Chev. (*cf.* Perrot, *l.c.* ; Anon., Imp. Inst. Col. Repts. Misc. No. 88, 1914, p. 543).

Among seed fats of the *Bassia* type may also be included **Katio Oil** from the Bornean *Ganua Motleyana* (De Vr.) Pierre (=*Bassia Motleyana* C. B. Clarke) (*cf.* Brooks, Analyst, 1909, **34**, 207; Anon., Imp. Inst. Col. Repts. Misc. No. 88, 1914, p. 551 ; Zimmermann, Chem. Weekblad, 1933, **30**, 657 ; the presence of small amounts of benzaldehyde and hydrocyanic acid in the oil from fresh seeds is reported) and the Burmese **Kanswe (Kansive) Oil** from *Payena oleifera* Watt ms. (Menon, J.S.C.I. 1910, **29**, 1428).

These fats are used locally to a considerable extent by the native populations for edible and other purposes ; up to the present, however, they have not been of any importance in the industrial or European markets. E. L.

BASSIA MAHWA or MOWRAH FLOWERS. The flowers of *B.* (Illipé) *latifolia* (Roxb.) or " Mahwa," a tree growing in great profusion in Central India. The flowers are very succulent and fall from the tree in large quantities every night throughout the season (approximately March and April). A single tree will yield between 200 and 400 lb. of flowers during that period. The dried flowers have been recommended as a source of sugar. Negri (Rev. Chim. Med. Pharm. 2384) found in them about 58% of glucose. If fermented and subsequently distilled they will yield approximately 3·5 gallons of alcohol (about 6 gallons of proof spirit) per cwt. The spirit is of superior quality and, if the operations are performed with care, the resultant product closely resembles good Irish whisky. The spent flowers resulting from distillery operations are a nuisance in certain Indian localities and efforts have been made to use them commercially. By heating for four hours with dilute sulphuric acid approximately 11% of sugar may be obtained from the carbohydrates still present. By diluting the extract from the original flowers with that from the spent flowers, the additional sugar ferments completely, giving a proportionately higher percentage yield of alcohol.

The flowers, both cooked and raw, are also used as an article of human food. As a cattle food they are very suitable, the flesh of the animals, particularly pigs, being much improved and acquiring a delicate flavour, whilst the spent flowers from fermentation have been found to constitute a very satisfactory food for milch cattle. F. G. H. T.

BASSIA TALLOW *v.* BASSIA FATS (MOWRAH BUTTER).

BASSISTEROL *v.* BASSIA FATS (ILLIPÉ BUTTER).

BASSORIN *v.* GUMS and GUM TRAGACANTH.

BASSWOOD OIL. A fatty oil peculiar in that it is found in the *bark* of the tree *Tilia americana* L. (N.O. *Tiliaceæ*). From 1–10% of (edible ?) fatty oil has also been found in the wood and bark of certain other species of *Tilia* and *Betula* (birch, N.O. *Betulaceæ*) ; the amount of the oil, which appears to alternate with starch in the tissues, varies according to the season of the year, rising to a maximum in the winter whilst the starch content falls to a minimum. (*cf.* Niklewski, Beih. z. Bot. Zentralbl. 1906, **19**, I, 68 ; H. Thoms and Michaelis, Ber. deut. Pharm. Ges. 1916, **26**, 185). The presence of a semi-drying oil (iodine value 95) in the bark of *Tiliacora acuminata*, Miers (N.O. *Menispermaceæ*) is recorded by van Itallie and Steenhauer (Pharm. Weekblad, 1922, **59**, 1381). Glycerides, fatty acids, sterols, etc., can be extracted by ether from the wood of species of *Pinus* (Hibbert and Philips, Canad. J. Res. 1931, **4**, 1 ; *cf.* Kurth and Sherrard, Ind. Eng. Chem. 1931, **23**, 1156) ; in this connection it may be noted that a mixture of fatty and resinous acids is recovered from pine wood as " tall oil " (*q.v.*), a by-product of the sulphate-cellulose pulp process. E. L.

BASTNÄSITE. A fluocarbonate of cerium-metals $(CeF)CO_3$, long known as small yellowish masses with greasy lustre embedded between allanite crystals at the Bastnäs mine, Riddarhyttan, Sweden. It has also been observed as an alteration product of tysonite (CeF_3) in the granite of the Pike's Peak region in El Paso Co., Colorado. Recently large masses have been found in Madagascar in the weathered debris of pegmatite at Torendrika to the east of Ambositra and near Antsirabe. These have the form of rough hexagonal prisms of a yellow to reddish-brown colour. Some crystals show an easy separation parallel to the basal plane on which the lustre is then pearly, otherwise it is greasy in character. The crystals are optically uniaxial and positive. Sp.gr. 4·948. The mineral is difficultly attacked by hydrochloric acid, but is decomposed by sulphuric acid, with evolution of carbon dioxide and hydrogen fluoride. It is infusible before the blowpipe. L. J. S.

BATATAS, or Sweet Potatoes, the tubers of a member of the *Convolvulus* family of plants, variously described as *Ipsomœa batata*, *Batatas edulis*, and *Convolvulus batatas*. The batata is grown in tropical and sub-tropical countries and forms an important vegetable of diet. It is used in much the same manner as the ordinary potato. In America two varieties are common, one mealy and light-coloured is more favoured in the north, and the other, more moist and deep yellow in colour, containing a large proproportion of sugar, is more usual in the south.

Numerous analytical data recorded fall generally within the following ranges:

Water	58–75%
Protein	0·5–3·5%
Fat	0·2–1·5%
N-free extract . .	18·0–37·0%
Sugars	2·2–5·6%
Fibre	0·6–2·5%
Ash	0·6–1·5%

The carbohydrate of the fresh tuber is largely in the form of starch with smaller proportions of sucrose and reducing sugars. Neither maltose, mannose, galactose nor pentose is present (Miyake, J. Biol. Chem. 1915, **21**, 503). During storage starch is converted first into reducing sugars and subsequently into sucrose (Hasselbring and Hawkins, J. Agric. Res. 1915, **3**, 331 and 543 ; **5**, 509). Changes occurring during five months' storage are shown thus:

	Water.	Starch.	Reducing Sugar (as dextrose).	Sucrose.
Beginning	73·5	19·1	0·9	1·9
After 5 months	72·2	14·1	1·7	6·1

Culpepper and Magoon (J. Agric. Res. 1926, **33**, 627) examined sweet potatoes from the point of view of canning, and give further details of the effects of storage and of cooking on their composition.

	Freshly Dug.		Stored.	
	Raw.	Cooked.	Raw.	Cooked.
Total solids . .	28·6	27·8	29·1	30·6
Solids soluble in alcohol . . .	5·3	13·8	10·1	17·4
Total sugars (as invert) . . .	4·0	8·9	8·1	12·5
Reducing sugars (as invert) . .	1·0	5·7	1·9	6·1
Sucrose (as invert)	3·0	3·2	6·1	6·4
Polysaccharides, total . . .	18·4	11·6	15·2	10·6
Dextrin . . .	—	0·7	—	1·3

Apart from their value as a food sweet potatoes form a notable source of starch and alcohol. Analyses of the ash constituents are recorded by Joffa and Curtis (California Agric. Exp. Sta. Rep. 1893–4, 219) :

K_2O	Na_2O	CaO	MgO	Fe_2O_3
58·2	8·1	5·6	4·1	0·5

P_2O_5	SO_3	SiO_2	Cl
16·2	3·0	2·1	2·6

Traces of **Mn**, **Cu**, and **Zn** have also been reported.

Osé (J. Agric. Chem. Soc. Japan, 1933, **9**, 165) obtained two monoaminophosphatides from the dried tubers.

More recently Matlack (Science, 1935, **81**, 536) reports the presence of a phytosterolin, probably sitosterol glucoside and a phytosterol, probably sisterol.

The vines of the plant have been shown to contain a cyanogenetic glucoside yielding 0·014–0·019% of hydrocyanic acid, sufficient to cause fatal injury to animals. A. G. Po.

BATH BRICK. A brick made from deposits of siliceous and calcareous earth at Bridgwater, Highbridge, and elsewhere, and used for polishing metals.

BAUXITE. A clay-like aluminium hydroxide first noticed by P. Berthier in 1821 (*alumine hydratée des Beaux*), and named beauxite by A. Dufrénoy in 1847, and bauxite by H. Sainte-Claire Deville in 1861 ; this name being from the village Les Beaux, or Les Baux, near Arles, dep. Bouches-du-Rhône, in the south of France, where the material was found. This material came to be regarded as a distinct mineral species with the composition

$$Al_2O_3,2H_2O,$$

corresponding with Al_2O_3, 73·9%, and H_2O, 26·1% ; that is, intermediate between the definite crystallised species diaspore

$$(Al_2O_3,H_2O)$$

and gibbsite ($Al_2O_3,3H_2O$). It varies widely, however, in composition, owing to intermixture with quartz-sand, clay and iron hydroxide and it passes insensibly into clays, iron-ores and laterite. The variations shown by different analyses are : Al_2O_3, 30·3–76·9 ; H_2O, 8·6–31·1 ; Fe_2O_3, 0·1–48·8 ; SiO_2, 1·1–41·5 ; TiO_2, 1·6–4·0 (from table of analyses quoted by G. P. Merrill, "The Non-metallic Minerals," New York, 1910). (For other analyses of French bauxite, *see* H. Arsandaux, Compt. rend. 1909, **148**, 936, 1115 ; Bull. Soc. franç. Min. 1913, **36**, 70).

The material shows no indications of crystalline structure, being always compact or earthy, or often with a concretionary (pisolitic or oolitic) structure. In colour it ranges from white, through creamy and yellow, to brown and deep red. Under the microscope it usually shows optically isotropic, flocculent grains ; but occasionally microscopic crystals of diaspore, gibbsite, and boehmite (*q.v.*) can be distinguished optically, and the presence of these is confirmed by X-ray analysis. Bauxite is thus largely a mixture of colloidal aluminium hydroxides (for which the mineralogical name *kliachite* has been proposed by F. Cornu, 1909, and *sporogelite* by M. Kišpatić, 1912), with various iron hydroxides, clays, etc., and also the crystalloids, diaspore and gibbsite. Titanium dioxide, often present in small amounts (up to 10%), is also supposed to exist in a colloidal form for which the name *doelterite* has been suggested by A. Lacroix, 1913 ; but it may really be present as rutile, anatase, and ilmenite in a very finely divided state. Like laterite, bauxite is thus of the nature of a rock rather than a simple mineral. When subjected to metamorphic processes a gibbsite-bauxite is changed into a hard, compact diaspore-bauxite, as in the Kashmir deposits ; while corundum is the final product of metamorphism, as in the emery deposits of Greece.

In its mode of occurrence, and no doubt also in its mode of origin, it also shows wide differences. The extensive deposits in the south of France have the form of beds interstratified with limestones of Cretaceous age, or of irregular pockets in the limestone. Those of Co. Antrim and of the Vogelsberg and Westerwald in Germany are associated with laterite, and are interbedded with basaltic lava-flows (G. A. J. Cole, "The interbasaltic rocks (iron ores and bauxites) of north-east Ireland," Mem. Geol. Survey, Ireland, 1912). In Arkansas the bauxite deposits occur only in Tertiary areas in the neighbourhood of eruptive syenites, while in Alabama and Georgia they overlie ancient sedimentary rocks (H. Ries, "Economic Geology," New York, 6th ed., 1930). The frequent presence of pisolitic structures in the material and its association with limestones have led to the suggestion that bauxite has been deposited by hot springs containing aluminium salts in solution (probably aluminium sulphate from the decomposition of pyritous shales) where these have come into contact with limestone rocks. On the other hand, the material associated with laterite and basalt has, no doubt, been produced by the weathering under special conditions (the agency of bacteria has been suggested) in tropical climates of basalt or of other igneous and crystalline rocks. The leaching out of silica and alkalis has left a residue of aluminium and iron in the form of hydroxides. In other cases, as in the "terra rossa" of the Karst region in Yugoslavia, the material is a residue from the solution of beds of impure limestone.

In France the present source of supply is mainly in dept. Var ; and in America the production is confined to the states of Alabama, Georgia and Arkansas. Other producing countries are British and Dutch Guiana, Gold Coast, India, Rumania, Hungary, Italy and Yugoslavia. The French bauxite is roughly divided into three classes : (1) white bauxite, with 60% alumina, not more than 4% iron and no silica—this being used for the manufacture of aluminium salts and alum ; (2) red bauxite, with 60% alumina and 3% silica—used for the manufacture of aluminium ; (3) a special kind of white bauxite, with 45% alumina, a trace of iron and much silica—used for making refractory bauxite bricks. The greater part of the material is used in the manufacture of aluminium. It is also largely used as a filtering material in petroleum refining, in the manufacture of aluminate cements, and in America it is fused in the electric furnace to produce artificial corundum, which, under the name of *alundum*, is largely used as an abrasive agent.

References.—W. G. Rumbold, "Bauxite and Aluminium," Monographs on Mineral Resources, Imperial Institute, London, 1926 ; C. S. Fox, "Bauxite," London, 1927 ; S. I. Tomkeieff, Min. Mag. 1933, **23**, 477. L. J. S.

BAUXITE AS A REFINING AGENT.

From the very earliest times practitioners in the art of refining have recognised the remarkable capacity possessed by certain substances, particularly charcoal and various porous earths, for selectively absorbing from natural products in common use traces of impurities which impair the colour, odour or flavour of the material. Among the many substances which possess these absorptive properties to a high degree are bone charcoal, specially prepared vegetable charcoals, fuller's earth, floridin, certain clays of Californian and Japanese origin, silica and alumina. Some of the most effective of these belong to the category of inorganic gels which have been formed by the dehydration of a hydrogel such as silicic acid or aluminium or ferric hydroxides.

A very convenient gel is the mineral bauxite, which is a soft rock composed principally of hydrated aluminium and ferric oxides associated with varying amounts of silica, lime, titania and magnesia. The mineral in its natural state has no adsorptive qualities, but by roasting to an appropriate temperature most of the water of combination is expelled, whereby the peculiar porous structure is developed upon which the refining efficiency depends.

As a refining agent for petroleum, bauxite has marked advantages over many other substances which also possess adsorptive properties. The size of the pores and nature of the surface happen to be just appropriate for the purpose in view, namely, the adsorption of the organic sulphur compounds and colouring matter which it is desirable to remove from petroleum distillates.

The use of this material for decolorising kerosine and paraffin wax was adopted by the Burmah Oil Company many years ago.

The procedure used at the Burmah refinery was as follows. The bauxite was placed in cylindrical filters measuring approximately 8 ft. by 2 ft. 6 in., and holding about 1 ton, and the kerosine or wax was filtered through until the colour of the outcoming oil was no longer up to the required standard. The spent bauxite was then extracted with benzine in a Merz extractor by continued percolation (after the manner of the Soxhlet apparatus) until no further removal of the adsorbed coloured compounds could be brought about.

The extracted bauxite, after removal of adherent benzine, was then passed through a vertical furnace into which it was dropped from a hopper at the top and fell from one sloping firebrick plate to another until it passed out at the bottom. During the whole period of its passage it came into direct contact with the hot gases (mixed with excess of air) from an oil burner, which oxidised any carbonaceous matter or hydrocarbons remaining after the extraction. It was then cooled as quickly as possible, when it was seen to be as clean and bright as new bauxite. For decolorising paraffin wax, the filters were steam-jacketed in order to keep the wax in a molten state.

When it became necessary to purify kerosine which contained both coloured matter and odoriferous sulphur compounds, it was found that it was not necessary to remove the sulphur compounds by chemical treatment before using the bauxite for decolorising (though this procedure may still be preferable in certain circumstances on considerations of cost), and that an appropriate bauxite treatment would effect the double purpose.

It is now practically certain that the phenomenon is one of surface adsorption, and the action of bauxite upon sulphurous oils appears to be strictly analogous with known cases of true adsorption.

(1) Material such as roasted bauxite containing large numbers of microscopic pores is well known to possess a considerable surface area and consequent surface energy.
(2) When oil is allowed to come into contact with freshly-ignited bauxite a considerable rise in temperature is observed, due to the surface energy being converted into heat energy.
(3) Bauxite obeys Freundlich's rule.

Bauxite as a Polymerising Agent.—Like all substances possessing a structure consisting of ultramicroscopic capillary tubes, bauxite has the power to bring about chemical changes in compounds with which it comes in contact. This is mostly in evidence among unsaturated hydrocarbon compounds (*e.g.* pinene and amylene are converted into dipolymerides), and is also seen in the case of the sulphur compounds present in petroleum oils. Decomposition and polymerisation both take place, the intensity of the reactions being favoured by increase of temperature. A. E. D.

BAVENITE. This mineral was first described from Baveno, Piedmont, Italy, by E. Artini in 1901 as a hydrated calcium aluminium silicate. It has recently been found to contain about 3% **BeO**, and the formula is written $4CaO{\cdot}Al_2O_3{\cdot}BeO{\cdot}9SiO_2{\cdot}H_2O$. At Baveno it forms radiating tufts of white needles in the drusy cavities in granite. It has since been found at Mesa Grande in California as white fine-grained material resembling kaolin and forming an alteration product of beryl. Minute lath-shaped crystals are orthorhombic, sp.gr. 2·74 (W. T. Schaller and J. G. Fairchild, Amer. Min. 1932, **17**, 409 ; C. J. Ksanda and H. E. Merwin, *ibid.* 1933, **18**, 341). L. J. S.

BAY, ESSENTIAL OIL OF. The oil distilled from the leaves of *Pimenta acris* (Wight), *Myrcia acris* (D.C.), N.O. *Myrtaceæ*, a tree largely grown in the West Indies—especially in St. Thomas, Jamaica, etc. The oil is distilled into water, where it separates into two fractions, a light fraction distilling over rapidly and a heavy fraction distilling more slowly, the former floating on the water, the latter sinking. These two fractions are mixed to obtain a normal oil. The yield is about 1%.

Characteristics : sp.gr. 0·945 to 0·990 ; opt. rot. 0° to −4° ; n_D^{20} 1·500 to 1·520. Miscible with an equal volume of 95% alcohol, but becoming turbid on further addition of alcohol.

It contains eugenol, chavicol, methyleugenol, methylchavicol citral, myrcene, and *l*-phellandrene. Myrcene is an olefinic terpene which on treatment with acetic anhydride yields linalyl acetate and dipentene. The proportion of phenols is 55–68%. Oil of bay is used in the preparation of bay rum. C. T. B.

BAYER ACID, CROCEIN ACID, CROCEIC ACID. Also *acid of Schultz*, o-*acid of Claus and Volz*, *acid of Bayer's patents*, *Rumpff acid*. 2-Naphthol-8-sulphonic acid.

BDELLIUM. The name bdellium is somewhat loosely applied to several gum resins containing a little essential oil which are found associated with myrrh and which somewhat resemble it. There are African bdellium, Indian bdellium, opaque bdellium and the so-called perfumed bdellium, which may be identical with the so-called bisabol myrrh. They are all probably the product of various species of *Commiphora* and *Balsamodendron*. Bdellium occurs in larger fragments than genuine myrrh and is less aromatic. When genuine myrrh is extracted with ether and the ether evaporated, the film of resin gives a violet colour when exposed to bromine vapour or nitric acid. Bdellium does not yield this reaction. Bdellium yields from 10 to 35% of extract to petroleum ether. The acid value varies from 10 to 37 and the ester value from 45 to 95.

The following values have been recorded for bdellium :

	African.	Indian.
Acid value . . .	9·7 to 20·8	35·7 to 37·2
Ester value . .	69·3 to 96·4	46·8 to 48·5
Petroleum ether extract . . .	20·3 to 36·1%	13·3 to 16·6%
Alcohol extract .	74·3%	—
Acid value of alcohol extract .	28·3	—
Ester value of alcohol extract .	119·3	—

E. J. P.

BEAN. A general term applied to a wide variety of kidney-shaped seeds, usually restricted in common usage to edible seeds of various members of the *Leguminoseæ*, although in commerce seeds of castor, coffee, etc., are included as " beans." The food value of beans is largely associated with their high protein content, and in some cases, notably that of the soya bean, with the amount of oil which they contain.

Beans are utilised either in the green succulent condition, *e.g.* French beans, or, after removal of the shell, in dried form, *e.g.* haricot, horse and soya bean. In the carob bean the husk itself forms the valuable product. A number of species are also cultivated as green fodder for animals, the immature plants being used whole for this purpose. The Chinese germinate the Mung bean and cook the young sprouts after a few days growth.

Varieties more commonly met with include :

(1) Adzuki beans (*Phaseolus radiatus* or *P. angularis*), largely of Japanese and Chinese origin.
(2) Broad beans (*Vicia faba*), more common in temperate European countries. Field or horse beans grown for cattle-feeding are of a similar type.
(3) Carob or locust beans (*Ceratonia siliqua*), also known as " St. John's bread," are the " locust " of Biblical times.

(4) French or kidney beans (*Phaseolus vulgaris*). The "string" or "snap" beans of America, where the immature pods are cooked as in this country. "Shell" beans are the dried mature seeds. White-seeded varieties are included as dried haricot beans.

(5) Gram beans (*Dolichos biflorus*), an Indian species.

(6) Jack beans (*Canavolia ensiformis*), common in eastern sub-tropical areas and in southern United States.

(7) Lima beans (*Phaseolus lunatus*). The true Lima bean is described as the variety *macrocarpus*, although the dwarf types, which include the Java, Rangoon and Burma beans and the Sieva (or civet) bean, are frequently included in this general category.

(8) Mung beans (*Phaseolus aureus*), another eastern type. In some quarters the name has also been applied to *P. mungo*, a similar type and utilised in a similar manner. In America the latter is more generally referred to as the Urd.

(9) Soya, soy, or soja beans (*Glycine* [or *Soja*] *hispida*). Originally of Chinese origin, now grown widely in America and recently introduced with considerable success into Europe.

(10) Velvet bean (*Mucuna utilis* or *Stizlobium deerengianum*), usually grown as a fodder crop.

Analyses of the different beans vary considerably with variety and growth conditions. The subjoined table includes ranges of values where such data are available.

	Water.	Protein.	Fat.	N-free ext.	Fibre.	Ash.
Adzuki beans . . .	14·0	21·0	0·7	56·3	4·0	3·6
Broad beans . . .	7·9–17·9	17·7–31·5	0·8–3·3	41·2–59·0	2·9–18·2	1·7–4·7
,, ,, (hulls) .	0	7·0	1·0	37·8	52·4	1·7
Carob beans . . .	9·1–19·8	3·3–15·2	1·0–3·8	27·0–43·6	5·0–17·4	1·7–3·5
,, ,, (pods). .	3·7–24·7	2·0–7·2	1·2–4·0	24·5–48·4	3·1–15·3	1·8–3·9
French beans (1) .	83–91	1·7–2·8	0·2–0·4	5·1–12·6	1·2–2·6	0·7–0·9
,, ,, (2) . .	9·6–15·5	19·9–26·6	1·4–3·1	57·2–63·5	3·2–7·2	2·7–4·4
Gram beans . . .	0	26·4	2·32	62·3	5·5	3·5
Jack beans (seed) . .	11·1–15·5	23·8–31·5	2·1–3·9	42·0–50·8	5·4–8·6	2·4–3·2
,, ,, (hulls) . .	15·2	5·0	0·6	15·5	57·9	5·8
Lima (fresh) . . .	65–68	7·1–7·3	0·7–1·3	20·3–23·4	0·8–1·7	1·7–1·8
,, (dried) . . .	8·3–12·2	12·8–24·5	0·6–1·9	—	—	3·6–4·7
Mung beans . . .	9·2–14·7	17·8–24·7	0·8–2·7	51·4–62·3	1·5–5·8	3·0–4·4
,, sprouts . . .	82·4–93·8	2·5–7·6	0·1–1·1	3·0–6·7	0·3–0·9	0·3–1·3
Urd beans	8·8–10·8	18·3–22·6	0·6–4·9	54·1–62·5	4·9–5·8	2·9–4·4
Soya beans (*a*) . . .	9·9	36·5	17·5	26·5	4·3	5·3
,, ,, (*b*)	9–10	35–43	9·7–12·9	27–33	3·5–4·7	4·7–5·2
Velvet beans, whole .	9·7	17·9	4·4	49·6	14·1	4·3
,, ,, seeds .	7·0	25·2	5·8	52·6	6·0	3·4

Note.—(1) Green, succulent ; (2) air-dry beans. (*a*) American ; (*b*) German grown.

The composition of the mineral matter of the beans is frequently characterised by large proportions of potassium and phosphorus, smaller proportions of magnesium, sodium, and sulphates, and very little sodium, silica, or chlorides.

The proteins of beans have been examined in considerable detail by Osborne *et al.* (1894–1900) in America, and later by Osborne and Clapp (Amer. J. Physiol. 1907, **18**, 295) and by Finks and Johns (J. Biol. Chem. 1920, **41**, 375) and Johns and Waterman (*ibid.* 1921).

From *Phaseolus vulgaris* have been isolated phaseolin (16·45% N, 0·5% S), conphaseolin (15·7% N, 1·36% S), both globulins, and phaselin (14·6%N and 0·5% S), an albumin. Phaseolin is the principal protein (15% of the seed). According to Osborne, *Vicia faba* contains legumin and vicilin (together approx. 17·0%), legumelin (1·25%), and a proteose (0·5%). From the Jack bean Jones and Johns (J. Biol. Chem. 1916, **28**, 67) obtained two globulins, canavalin (16·7% N, 0·5% S) representing the majority of the protein matter present and concanavalin (16·5% N, 1·1% S). Among several globulins occurring in velvet beans is stizolobin (Johns and Finks, J. Biol. Chem. 1918, **34**, 429). In the soya bean glycinin is the dominant protein, with smaller proportions of glutelin and an albumin. Largely as a result of the nature of the proteins present, the addition of small proportions of bean flour to wheat flour frequently improves its baking qualities.

As typical examples of the carbohydrate constituents of beans may be cited the following :

	Sugars.	Dextrins.	Starch.	Pentosans.	Galactosans.	Cellulose.
French Bean	1·6–2·6	3·2–3·7	35	8·1–8·3	1·3	3·1
Soya Bean	3·0–4·5	3·1	0·5	5·0	4·9	3·3

These are typical of the two general classes of beans, viz. starchy varieties and oil-seeds.

In some classes of bean, notably the smaller Lima beans (*P. lunatus*), there occurs a cyanogenetic glucoside, phaseolunatin (Dunstan and Henry, Proc. Roy. Soc. 1903, **72**, 285) ; this is possibly identical with the linamarin of flax (Jorissen, Bull. Soc. chim. Belg. 1907, 799). The hydrocyanic acid is almost completely removed by boiling.

Bean oils are largely of the non-drying or semi-drying types (75–85% unsaturated acids), the principal acids represented being oleic, valeric, and palmitic (but no stearic). Stellwaag records the ether-extract of *Vicia faba* to have the following characteristics: saponification value, 188; neutral fats, 57·7%; free acids, 9·8%; lecithin, 21·3%. Choline and cholesterol are commonly present in bean oils and betaine has been detected in horse beans. Grimme (Pharm. Zentr. 1911, **52**, 1141) reports the analysis of a number of bean oils.

The carob is unique among the beans in that the pod contains much sugar, values varying from 7–43% of sucrose and 3–20% reducing sugars. The seeds contain less sugar but are richer in protein. Bourquelot and Hérissey state that the carbohydrates of the seed consist largely of mannan and galactan, together with a type of vegetable gum, "caroubin," which has found some use in colour-printing and dyeing. The seed also contains an enzyme capable of converting urea into ammonium carbamate (Wagenaar, Pharm. Weekblad, 1925, **62**, 397), a distinction from the urease of soya bean which carries the reaction a stage further producing ammonia and carbon dioxide.

Instances of cattle poisoning following the use of the velvet bean as a forage crop have been traced to the presence in the crop of dehydroxyphenylalanine (Miller, J. Biol. Chem. 1920, **44**, 481).

Recent work of Magistris and Schäfer (Biochem. Z. 1929, **214**, 401) on the phosphorus compounds of the broad bean indicates the occurrence of phosphatides and lecithides but not free lecithin, as was formerly supposed. The following analytical data for these substances are characteristic.

	Phosphorus.	Nitrogen.	Reducing Substances (as glucose).
Phosphatides	2·04–1·11	1·14–2·36	15·1–5·9
Lecithides	1·6–3·5	0·9–1·7	2·0–11·0

The soya bean stands out as providing the most varied of uses. With due precaution the young green crop may be used as a fodder, or for the making of ensilage. The ripe seeds are a valuable source of oil, the residual cake finding a market as a protein concentrate for animal feeding. The protein constituents may be utilised as a form of "vegetable casein" in plastics and for the preparation of gums. Soya bean "milk" is prepared by grinding the seed, water straining, and concentrating. The dried, powdered residue forms permanent emulsions with water and according to Reid (Chinese J. Physiol. 1934, **8**, 53) contains protein 28·6, fat 16·4, carbohydrate 47·2, ash 3·9, Ca 0·3, P 0·5, H_2O 3·62%.

A. G. Po.

BEAN OIL *v.* Soya Bean Oil.

BEARBERRY LEAVES. The dried leaves of *Arctostaphylos Uva-ursi*, a common shrub in the northern hemisphere. They contain arbutin, $C_{12}H_{16}O_7,\frac{1}{2}H_2O$, m.p. about 168°, a crystalline glucoside which hydrolyses to dextrose and hydroquinone; *ursone*,

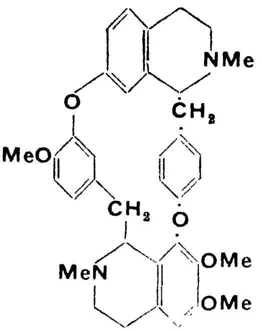
$$C_{38}H_{48}O_3,2H_2O,$$

crystals melting about 265°; methylarbutin, quercetin, probably myrecetin, tannin, gallic acid and ellagic acid. The infusion of the drug is an antiseptic, diuretic and astringent.

BEARING or ANTI-FRICTION METAL *v.* Antimony Alloys.

BEBEERINE, $C_{36}H_{38}O_6N_2$, is an alkaloid, first indicated in the bark of bebeeru or greenheart by Hugh Rodie, a naval surgeon, and used medicinally by the natives of British Guiana. This large tree, *Nectandra Rodiæi* Hook, is a source of valuable timber. Maclagan (Annalen, 1843, **48**, 106; Maclagan and Tilley, *ibid.* 1845, **55**, 105) isolated the alkaloid, which subsequent authors wrongly identified with *buxine* (*q.v.*). This older name was substituted for bebeerine until Scholtz (Arch. Pharm. 1898, **236**, 530; 1899, **237**, 199; 1906, **244**, 555; 1911, **249**, 416; 1913, **251**, 136; 1914, **252**, 513) disproved the supposed identity by showing that even quite impure bebeerine readily crystallises from methyl alcohol; it can then be crystallised from ethyl alcohol, but from no other solvent. On the other hand, Scholtz identified bebeerine with *pelosine* from *Radix Pareiræ*, which drug is derived from the Brazilian climbing shrub *Chondodendrum tomentosum* Ruiz et Pav., and most of the later work was done on material from this root, which seems to vary greatly. Sometimes the mixture of alkaloids from *Radix Pareiræ* yields only traces and sometimes up to 30% of crystalline bebeerine, which is generally dextrorotatory, $[\alpha]_D$ +300° in methyl alcohol, like the alkaloid from greenheart, but may also be *l*-bebeerine, identical with curine (*q.v.*). Both the *d*- and *l*- varieties melt at 214°, but *r*-bebeerine, obtained by mixing, melts at 299°–300°, and is much less soluble in alcohol than the active varieties. According to Scholtz (*l.c.* 1906), *d*-bebeerine is much more active pharmacologically than its enantiomorph; for the action of the latter, *see also* Hauschild, Arch. exp. Path. Pharm. 1934, **174**, 742.

d-Bebeerine is bitter and is obtained in a yield of 1% from greenheart bark and forms small glassy prisms (from methyl alcohol). Until recently a formula with eighteen carbon atoms was assigned to it, but Späth and Kuffner (Ber. 1934, **67** [B], 55) have shown that it is $C_{36}H_{38}O_6N_2$, and contains two *iso*quinoline nuclei, like oxyacanthine, *iso*chondodendrine, and other alkaloids from botanically related plants. Bebeerine yields a dimethiodide, m.p. 268°–270°, a diacetyl derivative, m.p. 147°–148°, a dibenzoyl derivative, m.p. 139°–140°. It contains two phenolic hydroxyls, two methoxy groups, and two bridge oxygen atoms. Zinc dust distillation yields 1-methyl-*iso*quinoline, potash fusion *p*-hydroxybenzoic and protocatechuic acids; Hofmann degradation of the dimethyl ether yields 2 : 3-dimethoxy-1 : 1′-diphenylether-5 : 6 : 4′-tricarboxylic acid. Hence Späth and Kuffner have suggested the annexed formula, in which the positions of the methoxyl and phenyl ether groups in the left half of the molecule are unknown, as are those of the free phenolic groups in bebeerine itself.



G. B.

BECKELITE. A silicate of calcium and cerium-earths $Ca_3(Ce,La,Di,Y)_4(Si,Zr)_3O_{15}$, containing Ce_2O_3 28·1, La_2O_3 13·6, Di_2O_3 18·0, $(Y,Er)_2O_3$ 2·8,. ZrO_2 2·5%, etc. It occurs as wax-yellow grains and cubic crystals as an accessory constituent in a dyke rock associated with elaeolite-syenite in the Mariupol district on the Sea of Azov, South Russia. The crystals (½ cm. diameter) have the form of octahedra and rhombic-dodecahedra, and resemble pyrochlore in general appearance and physical characters, but they possess a cubic instead of an octahedral cleavage. Chemically, however, they are quite distinct from pyrochlore, containing no columbium, titanium or fluorine. Sp.gr. 4·15 ; hardness 5. L. J. S.

BECKERITE *v.* AMBER OR SUCCINITE.

BECQUERELITE. A mineral of the composition $UO_3{\cdot}2H_2O$, named by A. Schoep in 1922 after A. H. Becquerel (1852–1908). It occurs as yellow crystalline crusts and minute orthorhombic crystals as an alteration product of pitchblende in the Kasolo radium mine in Katanga, Belgian Congo. Violet crystals of ianthinite ($UO_2{\cdot}2H_2O$) from the same locality change to becquerelite on exposure to air. Becquerelite has also been detected amongst the alteration products of pitchblende at Wölsendorf in Bavaria. A dimorphous form of $UO_3{\cdot}2H_2O$, called schoepite, from Kasolo, is also orthorhombic, but differing from becquerelite in crystalline form and optical characters. A related " mineral X " from Great Bear Lake, Canada (C. Palache, Amer. Min. 1933, **18**, 20 ; 1934, **19**, 309) appears to be a third orthorhombic form of $UO_3{\cdot}2H_2O$.

L. J. S.

BEECH TAR. Dry distillation of beech wood yields a mixture of acetic acid (45%), charcoal (23%), gases (28%, including 20% carbon dioxide), and oil or tar (4%). The tar contains a mixture of phenols and aromatic ethers together with more complex compounds (Fisher, Dingl. poly. J. 1880, **238**, 55). Fromm (Annalen, 1927, **456**, 168) has isolated the substance *cerulignol*, 4-hydroxy-3-methoxystyrene, b.p. 236°–238°, which is the source of the blue colour produced when beechwood creosote is treated with barium or calcium hydroxide (Bordas and Touplain, Compt. rend. **1923**, **176**, 1328). Gratzel (Arch. Pharm. 1877 [3], **10**, 130, 520) states that ferric chloride colours the tar blue changing to brown. *See* CREOSOTE.

BEECHNUT OIL is derived from the seed-kernels of the common beech, *Fagus sylvatica* L., which contain from 30–45% of oil (*i.e.* about 20–28% on the whole nuts). The pale yellow " cold-drawn " oil expressed from the shelled kernels (yield about 10–15%) is used to some extent on the Continent as a culinary oil, whilst the oil expressed at a higher temperature may be employed as a burning oil : the edible oil is stated to have been used as an adulterant of almond oil. The following figures for a beechnut oil examined by Heiduschka and Roser (J. pr. Chem. 1922 [ii], **104**, 137) are typical : d_{15} 0·9221, acid value 2·4, saponification value 190·5, iodine value 111·0, unsaponifiable matter 0·8%. The fatty acids of the oil consisted of (approx.) : α-linolenic acid 0·4%, α-linolic acid 9·7%, oleic acid 80·7%, palmitic acid 5·1%, stearic acid 3·6%. The oil from the kernels of the Japanese beech (*F. sylvatica* L., var. *Sieboldi*, Maxim.) which has been examined by S. Higuchi (Bull. Forest Expt. Stat. Meguro, Tokyo, 1915 ; *cf.* J.S.C.I. 1916, 261) appears to be closely similar to the European product : it is stated to be used in Japan for food, and also as a lubricant, for which purpose, however, the oil is not well suited as it is a " semi-drying " oil, with weak drying properties. E. L.

BEET (*Beta vulgaris*) includes several varieties : (1) red, garden beetroot ; (2) the mangold or mangel-wurzel ; (3) the sugar beet. The cultivated beets are derived from the wild *Beta maritima* (*Chenopodiaceæ*). All are notable for the proportion of sucrose present in the thickened roots, amounting to 19–20% in the modern varieties of sugar beet obtained by careful breeding and selection.

Although sucrose is the principal carbohydrate of interest, smaller amounts of glucose, fructose, and raffinose are present, also pentosans, pectins, and cellulose. Starch is rarely detected.

The proportion of sugar present, especially in sugar beet, is partly attributed to hereditable factors, but is largely influenced by growth conditions and manuring. Thus heavy applications of nitrogen fertilisers tend to lower the percentage of sugar in beet, although perhaps the total yield of roots may be much increased by this treatment. Exceptionally dry seasons favour the production of more fibrous roots containing higher sugar and ash contents but normal percentage N. The gross yield of roots is markedly lowered under these conditions. Smolenski, discussing the quality of sugar beet (Gaz. Cukrown. 1934, **74**, 150), places varieties into one of two classes : (1) high sugar—lower yield, and (2) lower sugar—higher yield types. The former are generally characterised by the production of lower root/top ratios, lower weight per root, and higher sugar, cellulose, and nitrogen contents in the roots. That differences in the metabolism of the plants are concerned is shown by the fact that high-sugar types (1) contain less mineral matter but relatively more calcium and magnesium and less sodium and potassium than lower sugar types (2).

Sucrose is not evenly distributed in the root tissues but is relatively more concentrated in the zone about half-way between crown and tip, and there is a descending gradient from the central axis towards the periphery. The mechanism of the storage of sucrose in the roots has given rise to much discussion. Sucrose, glucose, and fructose are all present in leaves, but sucrose predominates in the roots. In a number of papers published by Colin (Rev. gen. biol. 1916–1917) the view is expressed that glucose and fructose are produced photosynthetically by day and yield sucrose. By night sucrose is inverted, the two simpler sugars being translocated as such and reconverted into sucrose in the crown of the root. More recent work of A. L. Kursanov (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R. 1933, **12**, 3, 26) indicates a similar chain of effects and shows further that the actual amount of sugar accumulating in the roots is controlled by the rate of sucrose synthesis in roots rather than by that of photosynthesis in the leaves. According to Knowles, Watkins, and Hendry (J. Agric. Sci. 1934, **24**, 368) the course of growth of sugar beet is marked by a steady increase in the percentage of reducing sugars in the dry matter of leaves and in sucrose in that of roots, whereas the percentage of sucrose in leaves and of reducing sugars in roots remains at a comparatively low and approximately steady level throughout. Van Ginneken and de Haan (Med. Inst. Suikerbiet. 1933, **3**, 131) show that there is a close relationship between the weight of roots (w) and their sugar content (g) expressed by the form $g^2/w=$const.

The nature of the nitrogen compounds of beet has not been fully established. The constituent amino-acids of the proteins include glutamic and aspartic acids and arginine. Among purine bases Von Lippman records xanthine, guanine, hypoxanthine, adenine and carnine. Allantoin has been reported by several observers. The amide-nitrogen fraction comprises asparagine, glutamine, vernine, guanidine, vicine and alloxantin. Stanek (Z. physiol. Chem. 1911, **72**, 402) reports the presence of betaine (approximately 1% in roots and 2·6% in leaves) and of choline although there is some doubt as to the occurrence of the latter.

Leaves of beet contain appreciable amounts of oxalic acid, which in sugar beet and mangolds may reach 8% of the dry matter (Stoklasa, Bied. Zentr. 1901, **30**, 393). Ryder (J. Home Econ. 1930, **22**, 309) records 0·6–0·7% in fresh beet greens. The acidity of beet juice appears to be due to the presence of citric, malic, tartaric, oxalic, malonic and succinic acids.

Small amounts of fatty matter are found, largely in the peripheral cells of cultivated beet roots and are regarded as a reserve material. Neville (J.C.S. 1912, **101**, 1101) obtained palmitic acid 8·7, oleic acid 36·1, and erucic acid 18·6%, from the ether extract of mangolds, together with two sterols, $C_{31}H_{58}O_2$ and $C_{29}H_{45}O_2$. Pavlas (Listy Cukrovar, 1929, **47**, 527) also records a sterol of the formula $C_{28}H_{46}O_2$.

The red pigment of garden beets is an anthocyanin, betanin, whereas the yellow pigment of sugar beet possesses the characteristics of a saponin.

General analyses of beet vary considerably with variety and cultural conditions. The following represent average values :

	Water.	Protein.	Fat.	N-free ext.	Fibre.	Ash.
Mangolds, Large [1] . .	89·2	1·2	0·1	7·2	1·0	1·2
„ Small [1] . .	86·7	1·1	0·1	10·4	0·8	0·9
„ American .	90·8	1·4	0·16	5·7	0·9	1·1
Sugar beet	75–85	1·3–1·7	0·1	5·7–21·1	0·8–1·5	0·7–0·9
Garden beet . . .	87·9	1·5	0·1	7·9	1·0	1·1
Sugar beet leaves . .	84·0	2·3	0·4	7·4	1·6	4·8
Mangold leaves . .	91·8	2·4	0·4	2·8	0·8	1·4

Note.—[1] European varieties.

Average analyses of the ash constituents quoted by Winter are :

	K_2O	Na_2O	CaO	MgO	P_2O_5	SO_3	Cl
Garden beet	39·0	7·9	4·4	2·7	8·0	—	—
Sugar beet	46·2	7·7	5·7	3·8	9·6	1·0	—
Mangolds	31·1	10·7	4·9	3·3	7·4	2·9	5·7

Traces of Al, Mn, Cu, Zn, I, and B are usually present. Sugar beet grown in the absence of boron show a marked tendency to develop a type of heart rot, and the addition of borax or boric acid to fertilisers is now becoming popular.

A. G. Po.

BEETLE (trade name). Urea-formaldehyde moulding powders made by Messrs. Beetle Products Limited. The name is also applied to certain other solid and liquid urea and thiourea formaldehyde condensation products made by the same firm. *See* article on UREA-FORMALDEHYDE PLASTICS.

E. E. W.

BEET-ROOT GUM *v.* GUMS.

BEHENIC ACID, docosoic acid, $CH_3\cdot[CH_2]_{20}\cdot CO_2H$, occurs in Parkia oil, ben oil, and peanut oil (Paranj-pe, J. Indian Chem. Soc. 1931, **8**, 767 ; Jantzen and Tiedcke, J. pr. Chem. 1930 [ii], **127**, 277) and is found in various hardened oils (*e.g.* fish, rape and train oils). It may be prepared by catalytic reduction of brassidic acid or purified erucic acid (Talenzeff, J. pr. Chem. 1895 [ii], **50**, 71 ; Meyer, Brod, and Soyka, Monatsh. 1913, **34**, 1113 ; Morgan and Holmes, J.S.C.I. 1925, **44**, 491T ; Sudborough, J. Indian Inst. Sci. 1926, **9A**, 67 ; Thomas and Mattikow, J. Amer. Chem. Soc. 1926, **48**, 968). The acid has m.p. 83°–84°, but solidifies at 76°–79° ; b.p. 306°/60 mm. (Talenzeff, *l.c.*). It forms acicular crystals soluble in alcohol (0·102% at 17°) and in ether (0·1922% at 16°) ; the sodium salt is difficultly soluble in water or in dilute aqueous alcohol. The ethyl ester has m.p. 48°–49° ; for values of its dielectric constant in relation to phase changes, *see* Buckingham (Trans. Faraday Soc. 1934, **30**, 377).

For a method of estimation based on the potassium chlorate equivalent of the potassium salt of the acid, *see* Grossfield (Z. Unters. Lebensm. 1929, **58**, 209).

Derivatives.—The *octa-* and *deca-*bromides exist in α- and β- modifications, the α-form being infusible and insoluble and the β-form soluble and low melting (Rudy, Z. physiol. Chem. 1932, **210**, 236). Esters of diiodobehenic acid are obtained by esterification of diiodobehenic acid or by iodination of esters of behenic acid ; the ethyl ester has m.p. 37° (D.R.P. 468021). Bromoiodobehenic acid, m.p. 38°, results from the addition of iodine bromide to erucic acid, and iodohydroxybehenic acid from the addition of hypoiodous acid (Holde and Gorgas, Ber. 1925, **58** [B], 1071). G. F. B.

BEIDELLITE. A clay mineral,

$$Al_2O_3{\cdot}3SiO_2{\cdot}nH_2O,$$

where *n* is about 4, probably orthorhombic, from Beidell, Colorado. A green variety forming a passage to *nontronite*,

$$(Fe_2O_3{\cdot}3SiO_2{\cdot}nH_2O),$$

is called iron-beidellite (E. S. Larsen and E. T. Wherry, J. Washington Acad. Sci. 1925, **15**, 465 ; C. S. Ross and E. V. Shannon, *ibid.* 467 ; H. Ries, "Clays," 3rd ed., New York, 1927, 73). L. J. S.

BELLADONNA (Fr. *Belledame*). The *Atropa belladonna* or deadly nightshade, Fam. Solanaceæ (*v.* SOLANACEOUS ALKALOIDS).

BELLADONNINE *v.* SOLANACEOUS ALKALOIDS.

BELLITE. This name has been used (W. F. Petterd, 1905) for an incompletely determined mineral, described as a chromo-arsenate of lead, and occurring as bright-red or yellow velvety tufts, or as powdery encrustations, at Magnet in Tasmania. L. J. S.

BELL METAL. An alloy of copper and tin used in the manufacture of bells. It contains from 80 to 75% copper, and is hard, brittle, and sonorous at ordinary temperatures. At a dull red heat it is malleable, but again becomes brittle at bright redness. Large bells are cast and allowed to cool slowly, gongs are hammered to shape at dull redness and then allowed to cool.

"BENGAL GUM" *v.* BABUL GUM.

BENGAL LIGHTS or INDIAN FIRE. The term "Bengal Light," although it is now sometimes applied to coloured lights of any tint, should rightly be used only for the "blue light." It is a white light of bluish tint, and received its name before the introduction of potassium chlorate into pyrotechny made possible the variety of colours in use to-day. It is usually composed of sulphur 7 parts, realgar 2 parts, and nitre 24 parts.

BENITOITE. This interesting mineral is titano-silicate of barium, $BaTiSi_3O_9$, and forms beautiful sapphire-blue, transparent crystals suitable for cutting as gems. The crystals afford the only known example (except Ag_2HPO_4, H. Dufet, 1886) of the ditrigonal-bipyramidal class. Sp.gr. 3·64–3·67 ; H. 6½. The dichroism is intense, the ordinary ray being colourless, and the extraordinary ray greenish-blue to indigo-blue. The mineral has been found only in San Benito Co., California, near the source of the San Benito river, the crystals occurring embedded in natrolite veins traversing schistose rocks (G. D. Louderback, 1907). L. J. S.

BENJAMIN, GUM *v.* BALSAMS.

BEN OIL is a pale limpid oil abundant in the seeds of the trees *Moringa pterygosperma* Gaertn. (syn. *M. oleifera*, Lam.) and *M. aptera* (Forsk.) Gaertn., which are indigenous to India, Arabia and Syria but are now widely grown in the Tropics.[1] The oil is used locally as a cosmetic, and to some extent for edible purposes, and has also been employed in the "maceration" process for the extraction of perfumes from flowers ; ben oil has frequently been recommended as a lubricant for fine machinery, for which purpose the oil from *M. aptera*, which deposits less "stearin" on standing, appears to be the more suitable. Specific gravities from 0·9127–0·9151 at 15°C., saponification values of 186·3–188·2, and iodine values of 65–72 have been recorded for genuine samples of ben oil ; an iodine value as high as 100 has been observed by Lewkowitsch for an authentic cold-pressed oil from Nigerian seed, but the genuineness of commercial ben oil which shows much higher iodine values (*e.g.* 110) is open to question.

References.—Lewkowitsch, "Chem. Tech. and Analysis of Fats, Oils, and Waxes," 6th ed., 1922, vol. II, 381 ; Analyst, 1903, **28**, 343 ; Anon., Bull. Imp. Inst. 1904, **2**, 117 ; *ibid.* 1930, **28**, 276 (oil from Egyptian *M. aptera*) ; Imperial Inst., Col. Repts., Misc. 1914, No. 88, p. 488. E. L.

BENTONITE. An impure clay mineral consisting largely of montmorillonite, and formed by the alteration of glassy volcanic ash. It was first recognized in 1898 in the Fort Benton shales in Wyoming, and it has since been found as thick-bedded deposits over a wide area in the western United States and Canada (H. Ries, "Clays," 3rd ed., 1927 ; S. I. Tomkeieff, Min. Mag. 1933, **23**, 475). The material possesses marked adsorbent properties, and is used for refining petroleum, as a filler for paints, distempers, soaps, and paper (*see* Colloid Symposium Monograph, 1925, ii, 99; R. B. Ladoo, U.S.A. Bureau of Mines, 1921, Publication 2289). L. J. S.

---

[1] In India itself the oil is but rarely prepared, but the root of the tree is used as a substitute for horse-radish, whilst the root-bark and leaves are employed in native medicine (Chandrasena, "Chemistry and Pharmacology of Ceylon and Indian Medicinal Plants," Colombo, 1936).

BENZACETIN. Trade name for the ethyl ether of acetaminosalicylic acid,

$$EtO{\cdot}C_6H_3(NHAc)CO_2H$$

Antineuralgic.

BENZACONINE *v.* Aconitine and the Aconite Alkaloids.

BENZAL CHLORIDE, *Benzylidene Chloride*, $C_6H_5{\cdot}CHCl_2$.

BENZALDEHYDE, $C_6H_5{\cdot}CHO$, benzoic aldehyde, ethereal, volatile or essential oil of bitter almonds, essence of bitter almonds. Benzaldehyde occurs free in the leaves of the cherry laurel (*Prunus laurocerasus*), bird cherry (*Prunus padus*), and peach (*Amygdalus persica*), and as the glucoside *amygdalin* in bitter almonds and the kernels of other stone fruits. On hydrolysis by the enzyme *emulsin* or by dilute acids, amygdalin breaks down into benzaldehyde, glucose, and hydrogen cyanide:

$$C_{20}H_{27}NO_{11}+2H_2O$$
$$=C_7H_6O+HCN+2C_6H_{12}O_6$$

Benzaldehyde was discovered in bitter almonds by Mortrès in 1803, but was first isolated and studied by Liebig and Wöhler in 1837 (Annalen, 1837, **22**, 1).

Preparation.—(1) From bitter almonds (or peach kernels) by steam distillation of the press cake left after extracting the fatty oil. The hydrogen cyanide which also comes over may be removed by fractional distillation or by shaking with milk of lime and ferrous sulphate (Liebig and Wöhler). To obtain benzaldehyde in its purest form it is precipitated as the bisulphite compound $(C_7H_6O{\cdot}NaHSO_3)_2,H_2O$, which is crystallised from water and decomposed with sodium carbonate (Bertagnini, Annalen, 1853, **85**, 183; Müller and Limpricht, *ibid.* 1859, **111**, 136). A method has also been described for purifying benzaldehyde by dissolving it in sulphurous acid and precipitating the bisulphite compound by adding potassium chloride (G.P. 154499; Chem. Zentr. 1904, II, 965). (2) *Synthetic.*—Benzaldehyde is now more usually prepared from toluene, either through the halogen derivatives or—to avoid the presence of chlorine compounds in the product—by direct oxidation. Benzyl chloride is oxidised with lead nitrate or copper nitrate (Lauth and Grimaux, Bull. Soc. chim. 1867 [ii], **7**, 105) or with an alkali dichromate (G.P. 347583). Benzyl bromide is oxidised by heating with an aqueous solution of calcium or sodium nitrate, and gives a very pure product (U.S.P. 1272522). A mixture of benzyl and benzal chlorides (or bromides) obtained by chlorinating (or brominating) boiling toluene can also be used, oxidation being effected by means of manganese dioxide (G.P. 20909). Benzal chloride is also converted into benzaldehyde by heating with milk of lime under pressure:

$$C_6H_5{\cdot}CHCl_2+Ca(OH)_2$$
$$=C_6H_5{\cdot}CHO+CaCl_2+H_2O$$

(Freund, Chem.-Ztg. 1927, **51**, 803). According to Espenschied (G.P. 47187), the reaction takes place at ordinary pressure if insoluble substances such as chalk or barium sulphate are added to produce an emulsion.

Toluene may be oxidised directly to benzaldehyde by means of manganese dioxide (Raschig, Chem.-Ztg. 1900, **24**, 446; Shenderovich and Livshits, J. Chem. Ind. (Russia), 1929, **6**, 1439; B. 1930, 980), or electrolytically (Mann and Paulson, Trans. Amer. Electrochem. Soc. 1925, **47**, 3), or catalytically using especially the metals of Group V of the Periodic System (except vanadium) and the oxides of metals of Groups V and VI (Chem. Age, 1922, **7**, 410; Maugé, Rev. Gén. Mat. Col. 1922, **27**, 142; B.P. 189091, 189107; Swiss P. 88382; U.S.P. 1589632). Benzyl alcohol or its substitution products can be oxidised to benzaldehyde by means of sodium hypochlorite (Benedetti and Vanselow, U.S.P. 1405261) or by nitrobenzene, quinoline, dinitrobenzene, and copper oxide (Zetzsche and Zala, Helv. Chim. Acta, 1926, **9**, 288). Benzaldehyde has also been prepared by the electrolytic reduction of benzoic acid or its salts (G.P. 123554; Mettler, Ber. 1908, **41**, 4148) or of a solution of phenyl acetate (G.P. 138442).

Properties.—Benzaldehyde is a colourless liquid, f.p. −13·5° and b.p. 179°–180°; $d_4^{30}=1{\cdot}0365$; $d_4^{14}=1{\cdot}0567$. It has a characteristic bitter almond-like odour and is said to be somewhat poisonous, though the poisonous properties of ordinary oil of bitter almonds are mainly due to the presence of hydrogen cyanide. It is soluble in water to the extent of one part in 300, and miscible in all proportions with alcohol and ether. It has a high refractive index, values of which for various wavelengths have been determined by Feussner (Z. Physik, 1927, **45**, 689) and Pound (J. Physical Chem. 1931, **35**, 1496). Its magnetic rotatory power has been studied by Perkin (J.C.S. 1896, **69**, 1064).

Benzaldehyde readily undergoes oxidation in air to form benzoic acid, probably through perbenzoic acid (Van der Beek, Rec. trav. chim. 1928, **47**, 286). This oxidation is accelerated by small quantities of inorganic salts convertible to per-salts, and inhibited by hydrogen cyanide, which is sometimes added to synthetic benzaldehyde for that purpose (Dusart, Bull. Soc. chim. 1867, **8**, 459). Kuhn and Meyer (Naturwiss. 1928, **16**, 1028) claim to have obtained benzaldehyde in such a state of purity that it does not undergo autoxidation. Taken internally, benzaldehyde is oxidised to hippuric acid and benzamide. With aqueous caustic potash the Cannizzaro reaction occurs, giving benzoic acid and benzyl alcohol. According to Lachman (J. Amer. Chem. Soc. 1923, **45**, 2356), benzyl benzoate is the primary product. Benzaldehyde can be reduced by sodium and absolute alcohol to toluene and hexahydrobenzoic acid (Pommereau, Compt. rend. 1922, **174**, 685); if sodium ethoxide is used, benzoic acid and benzyl alcohol are the first products. With hydrogen and activated magnesium or platinum black, it is reduced to benzyl alcohol; the addition of a minute quantity of ferrous or ferric chloride prevents the rapid loss of activity of the platinum black and accelerates the reaction (Lüttringhaus, G.P. 384351 ; Carothers and Adams, J. Amer. Chem. Soc. 1923, **45**, 1071). With a nickel catalyst at 210°–235° the product is a mixture of benzene, toluene, and their hexahydrides.

When warmed with alcoholic potassium cyanide, benzaldehyde is converted into benzoin, $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_5$. It forms crystalline compounds with the bisulphites of the alkali metals. Under the influence of dehydrating agents benzaldehyde readily undergoes condensation with various other substances ; thus cinnamic acid is produced by heating it with acetic anhydride and dry sodium acetate (Perkin, J.C.S. 1877, **31**, 389) or with ethyl acetate and sodium ethoxide (Claisen, Ber. 1890, **23**, 976 ; Farbw. vorm. Meister, Lucius, w. Brüning, G.P. 53671),

$$C_6H_5{\cdot}CHO+CH_3{\cdot}COOH \\ =C_6H_5{\cdot}CH : CH{\cdot}COOH+H_2O$$

It combines with hydrazine to form benzalazine, $C_{14}H_{12}N_2$, which, on distillation, yields stilbene, $C_6H_5{\cdot}CH : CH{\cdot}C_6H_5$. It condenses with aniline to form benzylidene-aniline (Schiff's base), and with dimethyl aniline in the presence of zinc chloride it forms the compound

$$C_6H_5{\cdot}CH : CH(C_6H_4{\cdot}NMe_2)_2,$$

the leuco base of benzaldehyde green (Fischer, Ber. 1878, **11**, 950). With pyrogallol, benzaldehyde forms dyestuffs of the triphenylmethane series (Hofmann, Ber. 1893, **26**, 1139), and with chloracetopyrogallol a golden-yellow dyestuff (Kusselkaul and Kostanecki, Ber. 1896, **29**, 1886). By heating benzaldehyde with a little sulphur in a sealed tube, stilbene and benzoic acid are formed (Barbaglia and Marquardt, Ber. 1891, **24**, 1881).

Impurities and Adulterations.—Benzaldehyde very frequently contains hydrogen cyanide, either originally present or subsequently added (*v. supra*), and benzoic acid formed by spontaneous oxidation. The synthetic product usually contains chlorinated benzaldehydes. Alcohol, ethereal oils and nitrobenzene are sometimes fraudulently added ; the latter substance resembles benzaldehyde in odour.

To test the purity of a sample of benzaldehyde, the sp.gr. and b.p. should first be determined. The sample should also dissolve without residue in a solution of sodium bisulphite. Of the impurities above mentioned, hydrogen cyanide may be detected by distilling the oil and submitting the first portions of the distillate to the Prussian blue test ; chlorine compounds by heating the oil with metallic sodium or fuming sulphuric and nitric acids and testing for chloride (taking care, however, to distinguish between silver chloride and silver cyanide which will be formed if hydrogen cyanide or nitrobenzene be present) ; alcohol by the iodoform test, and ethereal oils or nitrobenzene by their insolubility in sodium bisulphite solution. Bourgoin (Ber. 1872, **5**, 293) tests for nitrobenzene by mixing the sample with twice its volume of caustic potash ; if nitrobenzene is present the mixture turns green, and on adding water it forms two layers, the lower yellow and the upper green, the latter turning red on standing for some hours. Benzoic acid in benzaldehyde may be estimated by shaking 50 c.c. of the sample with water and 10 c.c. *N*-sodium hydroxide, the excess alkali being then titrated back with *N*-acid, using phenolphthalein as indicator.

Uses.—Benzaldehyde is used for the manufacture of dyes and in the preparation of perfumes.

Detection and Estimation.—In addition to the usual aldehyde reactions, the following can be used as tests for benzaldehyde : the formation of a yellow compound with benzidine (van Eck, Pharm. Weekblad, 1923, **60**, 1204) ; a blood-red coloration with pyrocatechol (Tikkanen, Farm. Notisblad, 1927, No. 5 ; Chem. Zentr. 1932, II, 2213). Microchemical detection in fruits can be carried out by means of *p*-nitrophenylhydrazine chloride in 15% acetic acid. When a drop of this liquid is hung in benzaldehyde vapour, yellowish-brown crystals are formed (Griebel, Z. Unters. Nahrungs-u. Genussmittel, **47**, 438 ; Chem. Zentr. 1924, II, 1754 ; *see also* Griebel and Weiss, Mikrochem. 1927, **5**, 146).

Benzaldehyde may be estimated by heating the sample containing the benzaldehyde on the water-bath for half an hour with a reagent consisting of 1 c.c. of freshly distilled phenyl hydrazine and 0·5 c.c. of glacial acetic acid dissolved in 100 c.c. of distilled water. After standing for 12 hours the phenyl hydrazone is filtered through a Gooch crucible, dried over conc. sulphuric acid, and weighed. Weight of precipitated phenylhydrazone multiplied by 0·5481 gives the weight of benzaldehyde present in the original sample. Small quantities may be estimated satisfactorily by this method (Hérissey, J. Pharm. Chim. 1906, **23**, 60 ; Dennis and Dunbar, J.S.C.I. 1909, **28**, 488). Benzaldehyde may also be estimated colorimetrically by means of fuchsine decolourised with sulphurous acid (Woodman and Lyford, J. Amer. Chem. Soc. 1908, **30**, 1607) or, like other aldehydes, by oxidation to the corresponding acid by means of Nessler's reagent (Bougault and Gros, Bull. Soc. chim. 1922 [iv], **31**, 1348).

SUBSTITUTION DERIVATIVES OF BENZALDEHYDE.

Sulphonic Acids.—Benzaldehyde *o*-sulphonic acid (Kafa, Ber. 1891, **24**, 791 ; Wallach and Wüster, Ber. 1893, **26**, 150 ; Gnehm and Schüle, Annalen, 1898, **299**, 347 ; G.P. 88952) and benzaldehyde *p*-sulphonic acid (Farb. vorm. Sandoz, G.P. 154528) are important as the parent substances of various dyestuffs.

o-*Nitrobenzaldehyde.*—This may be prepared by the oxidation of the *di*-mercury derivative of *o*-toluene (Reissert, G.P. 186881 ; Kalle and Co., G.P. 199147) ; by the oxidation of *o*-nitrotoluene by passing the vapour over manganese dioxide at 210°–250° (Gilliard, Monnet, and Cartier, G.P. 101221 ; Bad. Anil. u. Soda Fab., B.P. 21947) or by means of nickel oxide, nickel chloride and hypochlorite (Bad. Anil. u. Soda Fab., G.P. 127388) ; by oxidation of nitro-

benzylaniline; by the oxidation of *o*-nitrobenzyl alcohol and its esters (Fischer, G.P. 48722; Kalle and Co., G.P. 104360, 106712); by oxidising *o*-nitrotoluene with a mixture of acetic anhydride, acetic, sulphuric, and chromic acids (Thiele and Winter, Annalen, 1900, **311**, 356; Fried. Bayer & Co., G.P. 121788) and hydrolysing the *o*-nitrobenzaldehyde diacetate thus obtained; or by the oxidation of the sodium salt of *o*-nitrophenylnitromethane by aqueous potassium permanganate at low temperatures (Soc. Chim. des Usines du Rhône, G.P. 237358).

o-Nitrobenzaldehyde is a yellow solid which, according to Brady and Harris (J.C.S. 1922, **123**, 484), exists in two forms. The stable *a*-form melts at 43·5° and is converted into the *β*-form melting at 40° by melting, cooling quickly and scratching with a platinum wire. The *β*-form gives large, transparent crystals which soon show opaque spots due to re-conversion to the *a*-form.

o-Nitrobenzaldehyde in solution oxidises in light to *o*-nitrobenzoic acid; when treated with acetone and caustic soda it yields indigotin (Baeyer, Ber. 1882, **15**, 2856). It condenses with methyl- and ethyl-aniline or their sulphonic acids to form leuco-bases of blue-green triphenyl methane dyestuffs (Clayton Aniline Co., G.P. 108317).

m-*Nitrobenzaldehyde*.—This may be prepared by dissolving one volume of benzaldehyde in a mixture of five volumes of fuming nitric acid and ten volumes of sulphuric acid, precipitating by the addition of water and recrystallising from dilute alcohol (Widmann, Ber. 1880, **13**, 678; Bertagnini, Annalen, 1851, **79**, 260). According to Brady and Harris (J.C.S. 1922, **123**, 484) direct nitration of benzaldehyde gives *m*- and *o*-nitrobenzaldehyde, with very little, if any, of the *p*-compound.

m-Nitrobenzaldehyde forms pale yellow needles, m.p. 58°. It condenses with the sulphonic acids of the tertiary aniline bases, giving dyestuffs (Kalle & Co., G.P. 73147).

p-*Nitrobenzaldehyde*.—This is prepared by methods similar to those used for the *o*-compound (G.P. 91503, 92084, 93539; Frdl. iv, 129) and by heating *p*-nitrobenzyl alcohol with copper oxide or other metallic oxides (Schmidt, G.P. 15881).

It forms colourless prisms, m.p. 106°. It can be condensed with benzene and its homologues to form *p*-triphenylmethane (Stolz, G.P. 40340); with secondary and tertiary amines to form alkyl- and aryl-derivatives of *p*-nitrodiaminotriphenylmethane (Fischer, G.P. 16766, 16707), and with the sulphonic acids of tertiary aniline bases (Kalle & Co., G.P. 73147).

The *o*-sulphonic acid of *p*-nitrobenzaldehyde is prepared by the oxidation of *p*-nitrotoluene-*o*-sulphonic acid and is a source of triphenylmethane dyestuffs (Green and Wahl, B.P. 21825).

2:4-*Dinitrobenzaldehyde* has been prepared by Sachs (Ber. 1902, **35**, 1228) by condensing 2:4-dinitrotoluene with *p*-nitrosodimethylaniline and decomposing the resultant product with acid.

o-*Chlorobenzaldehyde* is prepared by the oxidation of *o*-chlorotoluene with manganese dioxide and sulphuric acid (Gillard, Monnet, and Cartier, G.P. 101221), or by extraction from the products of incomplete chlorination of *o*-nitrotoluene (Kalle & Co., G.P. 110010, 115516). It has f.p. −4°, b.p. 208°/748 mm., and d^{8} 1·29 at 8°. By heating with a sulphite it is converted into *o*-chlorobenzaldehyde-3-sulphonic acid (Geigy & Co., G.P. 88952), which condenses readily with aromatic secondary and tertiary amines to yield dyestuffs of the triphenylmethane series (Geigy & Co., G.P. 94126). Sulphonation gives 1:3:6-chlorbenzaldehyde sulphonic acid, also a source of dyestuffs (Soc. Chem. Ind. Basle, B.P. 25128; Gnehm and Schüle, Annalen, 1898, **299**, 347).

m-*Chlorobenzaldehyde* is obtained from *m*-nitrobenzaldehyde by replacing the nitro-group by chlorine (Erdmann and Schwechten, Annalen, 1890, **260**, 259; Eichengrün and Einhorn, *ibid.* 1891, **262**, 135). It crystallises in prisms, m.p. 17° and b.p. 213°.

p-*Chlorobenzaldehyde* is formed together with the *o*-compound in most preparations and may be separated from the mixture by fractional distillation (Farbw. vorm. Meister, Lucius, w. Brüning, G.P. 207157), or by sulphonating or nitrating the *o*-compound (Ges. f. Chem. Ind., G.P. 98229, 102745). It is a crystalline solid, m.p. 47·5° and b.p. 213°–214°.

2:5-*Dichlorobenzaldehyde*, m.p. 57°–58°, is obtained by the action of antimony pentachloride on benzaldehyde in the presence of iodine (Gnehm and Bänziger, Ber. 1896, **29**, 875; Schüle, Annalen, 1898, **299**, 34).

2:6-*Dichlorobenzaldehyde* forms colourless needles, m.p. 70°–71°, and has been used for the manufacture of triphenylmethane dyes (Anilinfarb. u. Extr. Fabrik., G.P. 199943).

2:3:5-*Trichlorobenzaldehyde* and 2:3:4:5-*tetrachlorobenzaldehyde* are used for producing dyes of the Malachite Green series (B.P. 251511).

p-*Aminobenzaldehyde*, m.p. 70°–72°, is the most important of the amino-derivatives. It is prepared by reduction of the nitro-compound or by heating *p*-nitrotoluene with sulphur and sodium hydroxide (Geigy & Co., G.P. 86874).

o-*Aminobenzaldehyde*, m.p. 39°–40°, and m-*aminobenzaldehyde*, are obtained from the crude nitro-compounds by reduction and separation by means of sodium hyposulphite (Bayer & Co., G.P. 218364).

p-*Dimethylaminobenzaldehyde* is best obtained by condensing *p*-dimethylaminobenzyl alcohol (from dimethylaniline and formaldehyde) with *p*-nitrosodimethylaniline and decomposing the product with nitrous acid (Ullmann and Frey, Ber. 1904, **37**, 859). It crystallises in colourless needles, m.p. 73°, and can be used for the manufacture of triphenylmethane dyes.

Benzaldehyde—Use of in Synthetic Perfumes.

Synthetic benzaldehyde is so nearly identical with natural oil of almonds that it has practically superseded it in synthetic perfumery, for which purpose it should be absolutely free from chlorine, which is present in the cheaper qualities, as this impurity tends to cause the product in which it is used to darken, especially when used in soaps. It is used wherever an almond note is required, and to round off many other perfumes. E. J. P.

BENZAMINE HYDROCHLORIDE. *Betacaine Hydrochloride, β-Eucaine Hydrochloride.* Trade name for 4-benzoyloxy-2 : 2 : 6-trimethylpiperidine hydrochloride, m.p. about 268° (decomp.). Local anaesthetic. Benzamine lactate which is more soluble is sometimes preferred.

BENZANTHRONE *v.* ANTHRAQUINONE DYESTUFFS.

BENZENE AND ITS HOMOLOGUES. The name benzene (*Benzol, Benzole*, Fr. ; *Benzol*, Ger.) was derived in its original form from that of gum benzoin, probably as *benzoin oleum*, hence benzole, which latter form is still in use amongst nearly all distillers and users of it both in this country and on the Continent. In more strictly scientific literature, however, the name *benzene* has now become generally accepted, and the systematic termination *-ene* is employed in the names of its various homologues, as toluene, xylene, cymene, etc. The Standardisation of Tar Products Tests Committee has recommended that the ending *-ole* be used when the hydrocarbon contains a proportion of homologous hydrocarbons as in the normal commercial product, the ending *-ene* being reserved for the pure compound.

Benzene was first isolated by Faraday in 1825 from the liquid condensed by compressing oil gas. Mitscherlich, D'Arcet, Kopp, and many others obtained benzene by various processes, but the first practical industrial process was that of Mansfield (J.C.S. 1849, **1**, 244), who isolated the hydrocarbon from coal tar, which now, together with coal gas, forms the principal source of benzene and its homologues.

The aromatic hydrocarbons occur generally only in small quantities in petroleum oil, although in a few such oils appreciable proportions may be present. Thus, Borneo straight-run petrol may contain up to 40%, of which about 7% is benzene, 14% toluene, 15% xylene, and 4% higher homologues (Kewley, J. Inst. Petroleum Tech. 1921, **7**, 209).

Petroleum residues such as are obtained by extraction of kerosene with liquid sulphur dioxide are cracked commercially to produce benzene hydrocarbons (Dunstan, B.P. 250701, 1925). More complex hydrocarbon oils produced from the distillation or pressure hydrogenation of coal may also be cracked to simple aromatic hydrocarbons. Thus, a 60–85% yield of benzene is claimed by cracking in the presence of hydrogen the higher fractions of oil obtained from the Bergius process (I.G. Farbenind. A.-G., B.P. 281298, 1926). Shimmura and Nomura (J. Fuel Soc. Japan, 1934, **13**, 29–31) claim a 70% yield of benzole from coke oven tar by hydrogenation under a pressure of 200–250 atmospheres, at a temperature of 480°–500°C. in the presence of Mo and W catalysts. Phenols present in low temperature tar are also convertible to benzene hydrocarbons by passing the vapours with hydrogen through sulphided or tinned iron tubes at 750°C. (Franz Fischer, Abh. Kennt. Kohle, 1924–1927, **8**, 545). Better results are obtained by heating with hydrogen under a pressure of about 200 atm. at 460°C. in the presence of certain catalytic substances, notably molybdenum and its sulphides, tungsten and cobalt sulphides (Brennstoff-Chem. 1930, **11**, 449). A 75–80% yield of benzole has been claimed by the hydrogenation of creosote under high pressure conditions (" Gas World," 1935, **102**, Coking Section, 3).

A process for the conversion of naphthalene and other polynuclear hydrocarbons into benzene has been patented by the I.G. Farbenind. A.-G. (B.P. 283600, 1926); *see also* Schmidt, Ufer, and Kronig (Canad. P. 268281–2, 1926); Varga (F.P. 683069, 1929); and benzene has also been obtained from low temperature tars and other sources (Fischer and Lessing, " Conversion of Coal into Oils," 1925, p. 119 ; Morrell and Egloff, Ind. Eng. Chem. 1925, **17**, 473).

According to I.G. Farbenind. A.-G. (F.P. 621550, 1927), hydrocarbons of the benzene series are produced by the catalytic dehydrogenation of gases containing methane, ethane, ethylene, and other hydrocarbon gases. The method is to pass gases such as brown coal gas, coke oven gas, natural gas, etc., over suitable catalysts (*e.g.* alkaline earth carbonates, silica gel, active carbons, etc.), at 500°–900°C. at pressures up to 1,000 atm. Similar patents have been taken out by I.G. Farbenind. A.-G. (B.P. 258608, 261393, 1925 ; 264827, 1926 ; 309199, 1927 ; 311899, 1928; 336234, 1929; G.P. 578778, 1930). Ramage (Can. P. 299495, 1930) claims high yields of aromatic hydrocarbons when water gas and olefinic gases are passed at ordinary pressure over reduced iron at 550°–800°C. Benzene has been obtained from acetylene by irradiating the gas with a quartz mercury arc at 270°–360° (Livingston and Schiflett, J. Physical Chem. 1934, **38**, 377), and by heating ethylene without the aid of catalysts in an electrically heated quartz tube at 600°–900°C. (Waterman and Tulleners, Chem. Zentr. 1930, **101**, 3670). Zelinsky (Ber. 1924, **57**, 264) claims a 74% yield of light tar containing nearly 49% of benzene from acetylene, using a wood charcoal catalyst at 650°C. Franz Fischer has also investigated the condensation of acetylene to aromatic hydrocarbons (Brennstoff-Chem. 1929, **10**, 279).

The principal source of benzene and its homologues still lies, however, in the products of the destructive distillation of coal and they are recovered both from the tar and from the gas. The yields per 1,000 gallons of high temperature tar are approximately 6 gallons of benzene, 4 gallons of toluene, and 6 gallons of xylenes, while from coal gas 1·5–3·0 gallons of benzole are obtained for each ton of coal carbonised, the exact quantity depending on the type of carbonising plant used.

Recovery of Benzole from the Products of Coal Carbonisation.—Crude benzole is recovered from coal gas by treatment with gas oil in scrubbers or washers, or by adsorption by active charcoal or silica gel, and these processes are described in full in the section on Coke Manufacture and Recovery of By-Products.

A description of the cyclic process of benzole recovery by active charcoal developed by the Gas Light & Coke Co. is given by Hollings and Hay (Gas World, 1934, **100**, 189; Chem. & Ind. 1934, **53**, 143). Methods have also been developed for recovery of benzole by cooling the gas (M. Frankl, B.P. 356889, 1930 ; Gas J. 1931, **195**, 797).

The benzene, toluene and xylene present in high temperature tar are concentrated in the light oil or crude naphtha fraction collected up to 170°C., when the tar is distilled. This oil is re-distilled and the distillate is collected in three principal portions : 82°–110°C., 110°–140°C., and 140°–170°C. respectively. All these fractions contain basic substances, such as pyridine, acidic substances such as phenol and other impurities. To remove these impurities the crude fractions are separately agitated, first with concentrated sulphuric acid, which dissolves out the basic substances and unsaturated compounds, and then with caustic soda to remove the phenols. After each treatment a wash with water is given.

The washing processes are carried out in large iron or lead-lined vats fitted with a stirring device and baffles. Temperature control is effected by controlling the water supply to a jacket surrounding the vat. A typical form of apparatus is seen in Fig. 1.

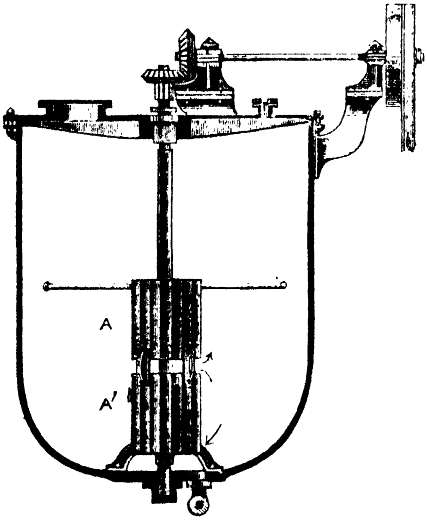


Fig. 1.

The details of the apparatus need no description except to point out that the screws used to force the fluids through the two vomiting tubes A and A′ should be set on the shaft with their helices reversed right and left, so that the lower one causes the lower fluid to rush up, and the upper one the upper fluid to rush down; the two currents thus meet violently, effecting thorough mixing. The central shaft may also consist of an Archimedean screw or of a truncated hollow cone. Air agitation is not advisable on account of the loss of benzole which it is apt to cause.

If the fraction is of fairly good quality and has been properly separated from the light oils, the amount of concentrated acid required (84% H_2SO_4) need not be more than one-twentieth of its weight. In some cases, however, where the impurities are difficult to remove more must be used, and the operation repeated. Where it is desired to recover the pyridine base, the washing with concentrated acid may be preceded with a wash with dilute acid (10% H_2SO_4).

Many modifications have been made to the acid washing process and an interesting development is suggested by continuous washing plants recently invented in which the benzole is vaporised and bubbled through the acid or passed in liquid form or as vapour through packed towers down which the acid flows (Mezger, Gas- u. Wasserfach, 1921, **64**, 825 ; Soc. du Gaz de Paris, B.P. 307935, 330045, 314052, 1928). Another method makes use of turbulent flow conditions for effecting admixture of the benzole with the various washing media, the whole process being carried out continuously in a coil system (S.M.G. Co., B.P. 393934, 1931). Kattwinkel (Brennstoff-Chem. 1924, **5**, 5) adds boric acid to the sulphuric acid used for washing, whereby he claims to reduce the loss of benzole. Emulsifying troubles which are sometimes experienced when washing with alkalis and water subsequent to the acid treatment can, according to the A.-G. für Chemiewerte (B.P. 231900, 1924), be avoided by the use of alkalis adsorbed in kieselguhr.

An injector method of purification by H_2SO_4 is described by Tyulyunnikov, J. Chem. Ind. Russ. 1930, **7**, 600.

The effect of acid washing on the various constituents of benzole has been examined by Moehrle (Brennstoff-Chem. 1932, **13**, 6). The washed products obtained in this way are then re-distilled ; that obtained from the fraction collected between 82° and 110°C. consists principally of benzene and toluene, and is sold as 90% benzole ; that obtained from the fraction 110°–140°C. consists of the same hydrocarbons (but in different proportions) together with xylene and is sold as 50% benzole; "90% benzole" contains about 70% benzene, and "50% benzole" about 46% of benzene.

The oil from the fraction collected between 140°C. and 170°C. consists of xylene, *pseudo*-cumene, mesitylene, etc., and is seldom purified ; it is employed principally as solvent naphtha. The early demands for benzole for use in the aniline colour industry were confined to 30%, 50%, and 90% benzoles. These terms were understood to mean that 30%, 50%, or 90% by volume of the sample boiled below 100°C. Of these the 30% was mainly used for the production of aniline for red, and the 90% for aniline for blue.

The introduction of the aniline black printing processes and other improvements in the dye industry, however, slowly gave rise to a demand for a pure benzene, while, later on, a demand for toluene and xylene stimulated the improvement of the distillation process.

Mansfield (*l.c.*), after isolating the crude benzol from coal-tar, obtained perfectly pure

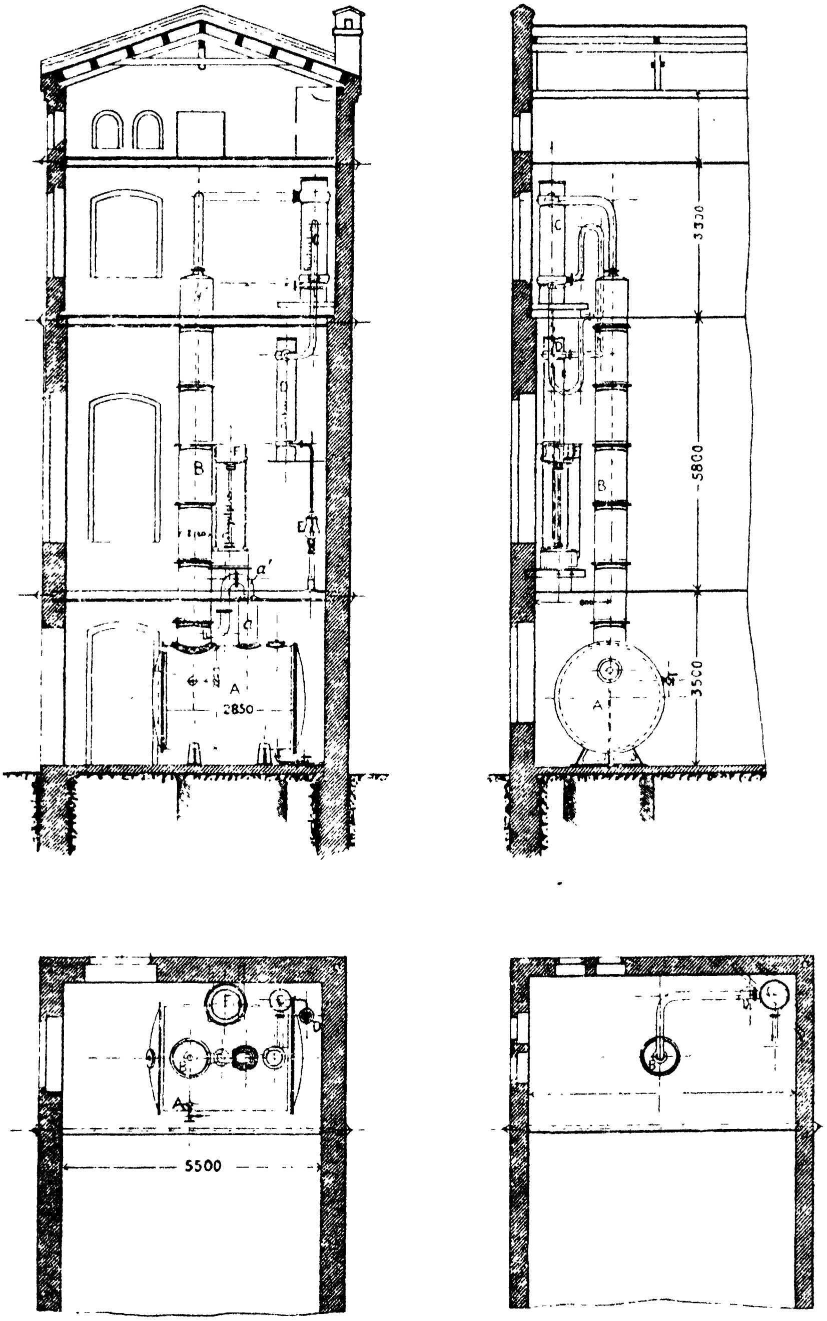


FIG. 2.

A, Still body. **B**, Analysing column. **C**, Cooler kept at required temperature of distillate.
D, Condenser for pure distillate. **E**, Glass sight gauge. **F**, Automatic regulator.

benzene by fractionation in glass retorts and finally by freezing and pressure. He made the observation: " It is evident that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits are applicable to the separation of benzole from the less volatile fluids of naphtha " (Reports of the College of Chemistry, 1848, 257).

Following on this suggestion of Mansfield's, developments in the distillation process led towards the use of such a still as had been introduced by Coffey in his patent of 1832 and subsequently carried to great efficiency by succeeding generations of spirit distillers. Coupier of Paris appears first to have worked on a large scale in this direction about 1863. He modified the original Mansfield apparatus and showed that in one operation he could separate ordinary 50% commercial benzole into the following fractions:

Distillation Temperature °C.	Distillation %
80 to 82 (" Pure benzole ") . .	44
82 „ 110 (Crude toluol) . . .	6
110 „ 112 (" Pure toluol ") . .	17
112 „ 137 (Crude xylol) . . .	5
137 „ 140 (" Pure xylol ") . .	9
140 „ 150 (last runnings) . . .	13–14

In addition, there was about 6% between 62° and 80°, consisting of various impurities such as carbon disulphide, acetonitrile, etc.

In Fig. 2 is seen a benzole still made by the Metallwerke vormals T. Aders, of Magdeburg-Neustadt. The still is charged with the selected fraction, which has undergone the necessary washings with sulphuric acid and sodium hydroxide, and steam is admitted into the heating coils.

As soon as the liquid begins to boil, the vapour ascends into the head *a* and passes through the curved tube *a′* into the bottom of the column B. This contains 25 to 30 flat diaphragms, each pierced with a number of small holes, and one larger, into which is fitted a short wide overflow tube, the end of which stands up about 2 in. above the level of the plate. On the opposite side of the plate is a small depression about 2 in. deep and 4 in. in diameter, into which the overflow tube from the plate above dips, its own tube dipping in the same way into a depression in the plate below.

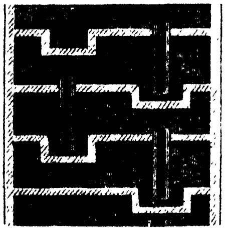


FIG. 3.

The condensed fluid acts as a trap (Fig. 3) to each overflow tube and prevents the ascent of vapour through it.

The rising vapour condenses rapidly on these plates, and the fluid thus produced, unable to penetrate the small holes through which the hot vapour is rushing, rises to the brim of the overflow tube, and then pours down from plate to plate into the still body. The non-condensed vapour rises through the perforations of the next plate, where it undergoes a similar operation, and so on to the top, the vapour passing away from which has thus been successively washed by bubbling through some thirty layers of fluid, each slightly cooler than the one beneath. Finally, the vapour passes through a surface or multitubular condenser, C, which is provided with a water supply so regulated that its temperature is about that of the boiling-point of the liquid required. The liquid here condensed flows back into the column at a suitable point, while the now purified vapour passes on to the second condenser, D, where it is finally completely condensed into the liquid form. Thence it flows through the glass sight gauge E, which is fitted on to a stand-pipe communicating with the distributing-pipes conveying the distillate to the store tanks.

After rectification in a still of this type, fractions are obtained as follows: benzene, b.p. 80°C.; toluene, 110°C.; xylene, 140°C.; the benzene and toluene should each distil constantly within 0·5° and 1·0° respectively, and the xylene within 2°. Pure benzene, to which a few drops of phenyl-hydrazine have been added, should give no crystalline precipitate on standing (test for carbon disulphide); when shaken with concentrated sulphuric acid it should be only slightly darkened (unsaturated aliphatic hydrocarbons); on shaking with sulphuric acid and a trace of isatin, no blue coloration should be produced (thiophen); on treatment with a mixture of nitric and sulphuric acids, and subsequent distillation in a current of steam, no unnitrated hydrocarbons should be obtained (paraffin hydrocarbons); lastly, it should solidify when cooled below 0°C.

Pure toluene of commerce should not impart any coloration to sulphuric acid when shaken with it. On shaking 90 c.c. of toluene with 10 c.c. of nitric acid (sp.gr. 1·44) in a stoppered bottle, the acid should assume only a red colour, and remain clear and bright, not turning greenish or blackish.

PHYSICAL PROPERTIES.

Benzene is a limpid, colourless, highly refracting liquid at ordinary temperatures. It exhibits no absorption lines or bands in the visible portion of the spectrum. Beyond *H*, however, photographs show a series of four bands covering the region lying between wavelengths 3171 and 2190 tenth-metres. The methyl substituted benzenes (toluene and the three xylenes) exhibit a similar absorption, very careful measurement indeed being required to distinguish one from the other (Hartley, J.C.S. 1885, **47**, 685; Proc. Roy. Soc. 1908, **80**, A, 162; Hartley and Dobbie, J.C.S. 1898, **73**, 695; Baly and Collie, *ibid.* 1905, **87**, 1332; Friederichs, Z. wiss. Phot. 1905, **3**, 154; Grebe, *ibid.* 376; Mies, *ibid.* 1909, **7**, 357; 1910, **8**, 287; Witte, *ibid.* 1915, **14**, 347; Massol and Faucon, Compt. rend. 1918, **166**, 819).

The physical constants of benzene together with those of toluene and *p*-xylene, have been given by Timmermans and Martin (J. Chim. phys. 1926, **23**, 747) in a report on the work of the International Bureau of Physico Chemical Standards.

	Benzene.	Toluene.	*p*-Xylene.
Boiling-point, °C.	80·20	110·80	138·40
Melting-point, °C.	5·493	−95·0	13·35
Density, 15°C.	0·88420	0·87160	0·86535
„ 30°C.	0·86844	0·85770	0·85230
Refractive index n_D 15°C.	1·50439	1·49985	1·49860
Viscosity (Poises × 10^5) 15°C.	696	623	682
30°C.	566	523	568

Baker (J.C.S. 1922, **121**, 568 ; 1928, 1051) has made the interesting discovery that the boiling-point of benzene can be raised to 106°C. by intensive drying over a period of several years with phosphorus pentoxide and has attributed this effect to molecular association. He gives the boiling-point of pure benzene dried over concentrated sulphuric acid as 79·6°C.

Benzene contracts on solidification, the difference in the specific volume of the liquid and solid ($v_f - v_s = \triangle v$) being between 0·1219 and 0·1304 at 5·35°C. (Heydweiller, Ann. Phys. Chem. 1897 [iii], **61**, 527).

For information relating to the freezing-points of mixtures of benzene and its homologues, reference should be made to the work of Ormandy and Craven (Proc. Inst. Auto. Eng. 1921–22, **16**, pt. 2, 143), and of Mitsukuri and Nakatsuchi (J. Soc. Chem. Ind. Japan, 1926, **29**, 25).

The following thermal data have been extracted from various publications :

	Benzene.	Toluene.	*m*-Xylene.
Heat of Combustion [1] g.-cal. at 18°C.	10,014	10,155	—
Specific heat [2] g.-cal. °C. at 30°C.	0·4095	0·3980	0·4010
Latent heat [3] g.-cal. at boiling-point	94·3	86·5	82·0

[1] Richards and Davis, J. Amer. Chem. Soc. 1920, **42**, 1599.

[2] Williams and Daniels, J. Amer. Chem. Soc. 1924, **46**, 903. (Curves relating to specific heat with temperature for benzene, toluene, and xylene.)

[3] Mathews, J. Amer. Chem. Soc. 1926, **48**, 562.

The heat of evaporation at temperatures other than boiling-point has been determined by Collins (J. Tennessee Acad. Sci. 1931, **6**, 17) who gives values of 102·5 g.-cal. at 24·2° and 94·4 g.-cal. at 80·2°C.

For observations on its thermal expansion, *see* Kopp (Jahresber. Ges. vaterl. Kultur, 1847–48, 66), Louguinine (Ann. Chim. Phys. 1867 [iv], **11**, 465), Adrieenz (Bull. Soc. chim. 1873 [ii], **20**, 280).

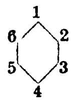
Benzene is an excellent solvent, dissolving caoutchouc, bitumen, plant-resins, sulphur, phosphorus, fats, oils, most of the natural alkaloids and many other organic compounds. Like CS_2, it dissolves iodine with the production of a violet solution. It is itself soluble to a very slight degree in water, considerably more so in alcohol, whilst ether, glacial acetic acid and carbon disulphide dissolve it readily.

The toxicity of benzene and its homologues (together with their nitro- and amino- derivatives) has been examined by Smyth (J. Ind. Hyg. 1931, **13**, 87). The vapour when inhaled produces giddiness and ultimately insensibility.

The physical properties of toluene, the monomethyl derivative, closely resemble those of benzene. As solvents they exhibit little or no difference, and though the boiling-point of toluene is so much higher than that of benzene, it evaporates nearly as rapidly in a current of air at ordinary temperature. The vapour of toluene has the same physiological effects as that of benzene. Xylene, the dimethyl derivative of benzene, exists in three isomeric forms, ortho-, meta-, and para-xylene; of the three, the meta- is chiefly used in commerce.

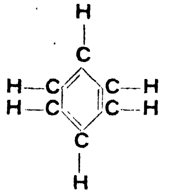
*ortho*Xylene boils at 141°–142°C., *meta-* at 139°C., and *para*xylene at 138·4°C. The two former are liquid at all temperatures down to at least −20°C. while *para*xylene melts at 13·4°C. The xylenes are appreciably less volatile than toluene and benzene in an air current. The smell of their vapours is unpleasant and pungent, and they possess the power of producing unconsciousness when inhaled. Mesitylene, the 1 : 3 : 5-tri-methyl derivative, is a colourless, mobile, pleasant-smelling liquid, boiling at 164·5°C. and volatile in steam.

Structure.—The constitution of benzene and its innumerable series of derivatives is usually represented by a regular hexagon of which each of the six angles represents a CH-group where substitution may take place.

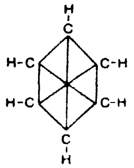


Since only one monosubstitution compound of a given kind (*i.e.* containing a given substituting group) is known, all the six CH-groups in benzene are assumed to be of equal value. The fact that disubstitution compounds exist in three distinct isomeric modifications (compare the above-mentioned *o*-, *m*-, and *p*-xylenes), is explained in this scheme by the following suppositions as to the relative positions occupied by the substituting groups. First, if substitution takes place at two adjacent angles, *e.g.* 1 and 2, 2 and 3, 4 and 5, etc., the word *ortho*- (*o*-) is prefixed to the name of the substance, as *ortho*-dimethylbenzene (commonly called *ortho*-xylene), or *ortho*dichlor-, *ortho*dibrom-, or *ortho*diaminobenzene, etc. If the substitution takes place at two angles not adjacent, but with one interposing, as at 1 and 3, 2 and 4, or 1 and 5, etc., the product is indicated by the prefix *meta*-, (*m*-), such as *meta*dimethylbenzene (commonly called *meta*xylene, etc.). Lastly, if the substitution takes place at opposite angles, such as 1 and 4, 2 and 5, 3 and 6, etc., the substance is known as a *para*- (*p*-) compound, as, for example, *para*dimethylbenzene, or *para*-xylene, *para*dinitro-benzene, etc.

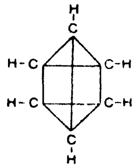
The hexagonal type of structure for benzene was first put forward by Kekulé who arranged the **CH**-groups as indicated in the following structional formula:



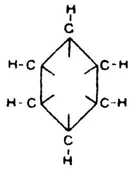
Other methods of disposing of the free valency bond of the **CH**-group have been put forward by Claus, Ladenberg, and Armstrong and Baeyer:



Claus
(Diagonal Formula)



Ladenburg
(Prism Formula)



Armstrong & Baeyer
(Centric Formula)

(For a resumé of work on the constitution of benzene, *see* Kauffmann, Chem. Zeitschr. 1905, **4**, 289; Holleman, Chem. Weekblad, 1915, **12**, 440.) (*See also* Colour and Chemical Constitution.)

Many new formulæ for benzene, including space models and electronic formulæ, have been devised recently in an attempt to account more satisfactorily for the general properties of the substance. Most of the electronic formulæ are based on the octet or Lewis-Langmuir theory. Of the 30 electrons in the benzene molecule, 12 are used in the union of carbon and hydrogen, and another 12 hold together the ring of carbon atoms; opinion differs as to the disposal of the remaining 6. Crocker (J. Amer. Chem. Soc. 1922, **44**, 1618) places these 6 electrons between the carbon atoms in the plane of the ring, thus forming an octet for each carbon atom. Orelkin (J. Russ. Phys. Chem. Soc. 1923, **54**, 493) suggests a symmetrical arrangement of the 6 spare electrons in the molecule in which they lie at the centres of the sides of two triangles on parallel planes, the apexes of which are formed by the nuclei of the carbon atoms which in projection give a regular hexagon. Morse (Proc. Nat. Acad. Sci. 1927, **13**, 789) describes a space model with the centres of the carbon nuclei and two sets of electrons arranged in three concentric spheres. Loewen (Z. Elektrochem. 1928, **34**, 760) depicts the benzene formula with four of the ring carbon atoms in one plane, and places the fifth carbon atom above this plane and the sixth in a para-position below the plane; he claims that this arrangement is in accordance with X-ray measurements. (Mrs.) K. Lonsdale (Proc. Roy. Soc. 1929, **123**, 494) finds, however, that X-ray examination of hexamethylbenzene reveals an hexagonal structure with all the carbon atoms and the methyl groups in one plane. Armstrong (Chem. and Ind. 1928, **47**, 894; 1929, **48**, 914) sees the benzene nucleus like a honeycomb cell cut from a sheet of diamond, but suggests the possibility of another arrangement in which the centres of the six carbon atoms may fall in one plane as apparently is the case with hexamethylbenzene, the hydrocarbon examined by Lonsdale. He is of the opinion that this hydrocarbon may be a derivative of an *iso*-benzene.

Chemical Properties.

Benzene forms an additive compound with picric acid, $HO{\cdot}C_6H_2(NO_2)_3{\cdot}C_6H_6$, which melts with decomposition at 90°C., and with triphenyl-methane, $CH(C_6H_5)_3{\cdot}C_6H_6$, melting at 75°C.

When strongly heated in sealed tubes or when passed slowly through strongly heated open tubes, condensation and decomposition go on together, acetylene, diphenyl, diphenyl-benzene, etc., being formed with evolution of hydrogen and deposition of carbon (Smith and Lewcock, J.C.S. 1912, **101**, 1453; Zanetti and Egloff, Ind. Eng. Chem. 1917, **9**, 350).

Oxidation.—Oxidising agents, such as potassium permanganate or manganese dioxide and sulphuric acid, convert it into formic, propionic and oxalic acids, together with small quantities of benzoic and phthalic acids, the two last named being produced by the simultaneous oxidation of formic acid and benzene, the process of condensation resembling that occurring in the conversion of dimethyl-aniline into methyl violet.

The oxidation of benzene by means of air in the presence of vanadium oxide catalysts at 400°C. has been examined with interesting results, and patents for the preparation of maleic acid by this method have been taken out by Weiss and Downs (Can. P. 192766, 1919; U.S.P. 1374720, 1921; *see also* Ind. Eng. Chem. 1920, **12**, 228).

Halogenation.—When chlorine acts on pure benzene in sunlight, an additive compound, benzene hexachloride, $C_6H_6Cl_6$, is formed. The substitution of chlorine for hydrogen in the nucleus or benzene ring is a very slow operation if chlorine alone is used, but if in every litre of benzene about 10 g. of iodine are dissolved, and the liquid kept boiling while a brisk current of chlorine is passed into it, substitution readily takes place and chloro-derivatives are produced. The addition of iron and aluminium as carriers also hastens the chlorination. The reaction may be continued until the whole of the hydrogen is replaced with the production of hexachlorobenzene, C_6Cl_6. Corresponding bromine and iodine compounds, and mono- and *p*-di-fluoro-derivatives are known. For the electrolytic chlorination of benzene and toluene, reference should be made to Van Name and Maryott (Amer. J. Sci. 1913 [iv], **35**, 153) and Fichter and Glantzstein (Ber. 1916, **49**, 2473). Chlorination of benzene and toluene in sectional glass towers by the influence of actinic rays has been patented by Conklin (Solvay Process Co., U.S.P. 1828859, 1923) and chlorination in the vapour phase by Mason, Smale, and Thompson (J.C.S. 1931, 3150).

Nitration.—When subjected to the action of strong nitric acid or a mixture of nitric and sulphuric acids, substitution of hydrogen by NO_2 takes place with great ease. If the mixture be kept cool only mononitrobenzene is formed, but if heated, the three dinitrobenzenes are produced, the *meta*dinitro-product (m.p. 89°C.) always greatly predominating. The *ortho-* and *para*-compounds can only be produced in quantity by indirect methods. Trinitrobenzenes can only be obtained by the action of a large excess of a mixture of nitric acid and fuming sulphuric acid.

A continuous process for the nitration of benzene in the presence of mercury compounds has been claimed by Brewster (U.S.P. 1380186, 1921).

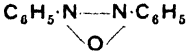
Schaarschmidt (Ber. 1924, **57**, 2065) uses as a nitrating agent synthetic nitrogen peroxide obtained from air or ammonia. The dry peroxide reacts with benzene in the presence of aluminium chloride or iron chloride, giving additive compounds, which are decomposed, forming the mono-nitro compound on addition of water. If benzene be treated with 59–60% nitric acid in the presence of mercury salts as catalysts, 2 : 4-dinitrophenol is obtained. The once used acid solution together with the catalyst, on making up the acidity by addition of concentrated nitric acid, can be used again several times with advantage, giving yields up to 80% (Zakharov, J. Chem. Ind. Russ. 1927, **4**, 960 ; 1928, **5**, 26 ; 1929, **6**, 698).

All the nitro-compounds on reduction with appropriate reagents, such as iron, zinc, or tin, in the presence of acid (preferably hydrochloric acid) and water, yield amino-compounds corresponding with the nitro-compound reduced (*e.g.* aniline, $C_6H_5{\cdot}NH_2$, the three diaminobenzenes or phenylenediamines, $C_6H_4(NH_2)_2$, etc.).

The amino-compounds, by the action of nitrous acid or nitrites in the presence of an excess of acid (preferably hydrochloric acid) are converted into diazo-compounds. If a diazobenzene salt, *e.g.* $C_6H_5{\cdot}N_2Cl$, is dissolved in absolute alcohol, and the solution heated, the nitrogen is evolved as gas whilst benzene is regenerated. If a diazo-salt is dissolved in water and boiled in the presence of an acid, nitrogen is also evolved and the corresponding phenol is produced. The diazonium salts also find important applications in their transformation into the nitrile or halogen derivatives in the presence of the corresponding cuprous salt (Sandmeyer reaction).

The diazo-compounds couple with certain amino-compounds or phenols, giving rise to the almost innumerable series of colouring matters known as azo-dyes (*q.v.*). Under proper conditions the diazo-compounds may attack the *amino*-group of amino-compounds, forming diazoamino-compounds such as diazoaminobenzene, $C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$. These can be made to undergo an isomeric change resulting in the formation of what are known as aminoazo-compounds, of which aminoazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$, is a typical example. Such substances, when treated with a reducing agent, split up into an amine and a *para*diamine, while diazo-compounds yield hydrazines only, and diazoamino-compounds a mixture of a hydrazine and an amine.

If the nitro-compounds are submitted to the action of alkaline reducing agents in alcoholic solution, such as a mixture of zinc-dust and alcoholic sodium hydroxide, the reaction takes a different course altogether. The action of alcoholic sodium hydroxide and heat alone will convert mononitrobenzene into azoxybenzene,



$C_6H_5{\cdot}N{-}N{\cdot}C_6H_5$ with O bridging below ; and this, by nascent hydrogen, is converted into azobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_5$, which under the action of the same reagent is still further reduced to hydrazobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. The latter, when boiled with an acid, is converted into a salt of benzidine (*para*diaminodiphenyl), $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, a base isomeric with hydrazobenzene.

Sulphonation.—When heated with concentrated sulphuric acid or treated in the cold with solutions of sulphur trioxide in sulphuric acid, benzene sulphonic acids are produced by substitution of the group —SO_3H for hydrogen. These are either mono-, di-, or poly-sulphonic acids, according to the condition of treatment (temperature, concentration of acid, etc.). They are all powerful acids, and form well-defined and generally well-crystallised salts with sodium, potassium, ammonium, and equally definite, though less easily crystallised salts with calcium, barium, copper, iron, etc. These salts, especially those of sodium or potassium, if fused with caustic potash or soda, or heated under pressure (40 atmospheres) with aqueous soda or potash, are decomposed with production of a sulphite of the alkali metal, and conversion of the benzene residue into the sodium or potassium salt of the corresponding hydroxy- or phenolic compound.

Hydrogenation.—The vapour of benzene mixed with hydrogen and passed over finely divided nickel heated to 170°–190°C. yields *cyclo*hexane, C_6H_{12} ; the homologues of benzene behave in a similar way. By passing dry ammonia through benzene containing calcium shavings a calcium-ammonia compound is formed, which with the benzene produces dihydrobenzene, C_6H_8.

$$Ca(NH_3)_4 = Ca(NH_2)_2 + 2NH_3 + H_2$$
$$H_2 + C_6H_6 = C_6H_8$$

(Dumanski and Zvereva, J. Russ. Phys. Chem. Soc. 1916, **48**, 994).

The hydrogenation of benzene to the hexahydro derivative is described by Kagehira (Bull. Chem. Soc. Japan, 1931, **6**, 241) and by Schoorel, Tulleners, and Waterman (J. Inst. Petroleum Tech. 1932, **18**, 179).

According to Holloway and Krase (Ind. Eng. Chem. 1933, **25**, 497), benzene heated with carbon monoxide under pressure in the presence of $AlCl_3$ gives benzaldehyde.

BENZOLE AS A MOTOR FUEL.

The use of benzene for the manufacture of refined chemicals and intermediate products for dyes is adequately treated elsewhere, and references will be found under the appropriate headings. Mixed with other homologues, the mixture being technically termed " benzole," its main use is as a motor fuel. It excels petrol as a source of power, especially for modern cars, because it will permit of very high compression ratios without knocking (Nash and Howes, Nature, 1929, **123**, 276, 639 ; J.S.C.I. 1930, **49**, 16T, 113T ; Ricardo, Report Empire Motor Fuel Ctte., Proc. Inst. Auto. Eng. 1923, **18** [i], 51). To facilitate starting, it is preferable, however, to use benzene in mixture with petrol.

Refining.—Crude mixtures of benzene and its homologues as produced in a normal distillation from coal tar or as obtained by various methods from coal gas show a marked tendency to form gumming deposits causing considerable inconvenience when the benzole is used in internal combustion engines. This gum-forming tendency can be eliminated by refining with concentrated sulphuric acid as already described, but it is now realised that such treatment is wasteful seeing that the unsaturated hydrocarbons which are thereby lost, themselves form excellent fuel. The efforts of recent workers have therefore been directed to methods of inhibiting the changes leading to gum formation. Resinification has been shown to be partly an oxidising and partly a polymerising process introduced by intermediate formation of active peroxides or peracids (Hoffert and Claxton, Rep. Joint Benzole Research Committee, 1928, 5 ; Brooks, Ind. Eng. Chem. 1926, **18**, 1198 ; Story, Provine, and Bennett, *ibid.* 1929, **21**, 1079 ; Wagner and Hyman, J. Inst. Petroleum Tech. 1929, **15**, 674) ; and it has been found that by the addition of certain anti-oxidants, gum formation may be completely arrested. Thus, according to the Benzole Research Committee (Report Joint Benzole Res. Ctte. 1926), the gum-forming tendency may be effectively suppressed by the addition of 1 part of cresol to 2,500 parts of benzole.

Hoffert and Claxton (Gas- u. Wasserfach, 1933, **76**, 704) regard phenols and aminophenols as the most valuable inhibitors and consider the addition of 0·03–0·05% of commercial cresol necessary for safety.

Hoffert (Chaleur et Ind. 1934, **15**, No. 167, 389) discusses very comprehensively the effects of gum formation and its prevention by inhibitors, 58 references being given.

Attempts to remove the less stable compounds responsible for gumming without entirely removing the unsaturated compounds have been less successful, but a much improved product can be obtained by such methods. Kruger (Gas Age Record, 1928, **61**, 577) after preliminarily washing the oil with a small amount of acid treats it with silica gel at 150°C., under a pressure of 50 lb. per sq. in. Geddes (Gas World 1931, **94**, Coking Section 9) emphasises the selective action of silica gel in polymerising the gum-forming constituents to high boiling resins. Others use gels or charcoals on which small amounts of acid have been adsorbed (Union Oil Co., B.P. 213881, 1923). Uloth (Brennstoff-Chem. 1929, **10**, 297) heats the oil under pressure with sulphur. A number of processes make use of the polymerising action of certain metals and their salts, such as iron or aluminium chloride (Supan, G.P. 394217, 1923) ; stannic chloride (Torossian, Ind. Eng. Chem. 1921, **13**, 903) ; zinc chloride (Popov and Polonskaya, Neftyanoe Khozyaistvo, 1933, **25**, 93) ; aluminium activated by mercury or salts of silver (d'Hercourt, F.P. 736378, 1931). In the Instill process (B.P. 269242 and 273883, 1926) an adsorbent clay impregnated with ferric sulphate is used at a temperature of 55°C. A description of this process in operation at the Rotherham Main Coke Ovens is given in Gas World, 1932, **97**, Coking Section, 125.

Other methods of refining include oxidation by electrolysing a slurry of benzene and weak sulphuric acid (Gludd, Löpmann, and Keller, Ber. Ges. Kohlentech. 1931, **4**, 82) ; hydrogenation (Rosendahl, Petroleum Z. 1932, **28**, No. 3, 12); oxidation by a slightly acid solution of potassium permanganate (Guillet, F.P. 761454, 1932); polymerisation by metallic chlorides preceded by or followed by silent electric discharges (I.G. Farbenind. A.-G., B.P. 409813, 1932).

Removal of Sulphur Compounds.—Both benzene and toluene when prepared from coal tar or coal gas are accompanied by sulphur compounds such as carbon disulphide and thiophens. Thiophen, C_4H_4S, was isolated in 1882 by V. Meyer, who obtained by constant and repeated agitation with sulphuric acid about 2 kilos from 2,000 kilos of commercial benzene. It is a colourless liquid, boiling at 84°C. ; d^{15} 1·100.

In many of its reactions it behaves like benzene. Two thiotolens (methyl thiophens) corresponding with toluene are known. They both boil at about 113°C.; *d* 1·0194.

Carbon disulphide is usually removed by very careful fractionation, it may also be removed by the Methanol Soda Process (Hoffert and Hancock, B.P. 416404, 428931, 1933; Gas World, 1935, **103**, 151). The benzene is extracted with caustic soda and methanol. The CS_2 is converted to methyl xanthate which on dilution with water can be removed from the benzene. The methanol is recovered by decomposing the xanthate with dilute acid, and distilling the aqueous portion. The carbon disulphide is recovered as a black liquid.

Even with the most careful distillation and rectification benzene obtained from refined benzole contains thiophen, and it is necessary that this should be removed before the benzene can be used for the preparation of pure chemicals and dye intermediates. Evans and Hollings (B.P. 152470, 1919) remove thiophen by washing with 60–85% sulphuric acid at 30°–90°C.

According to I.G. Farbenind. A.-G. (F.P. 655230, 1928), thiophen is removed by heating the benzene with hydrogen to 250°–300°C. at a pressure of 50–100 atm. in the presence of a sulphur stable catalyst such as molybdenum sulphide or a mixture of chromium oxide and nickel sulphide.

Thiophen may also be removed by stirring the benzene with red mercuric oxide and stearic acid at 80°C. for 90 minutes, and then distilling off the pure benzene, leaving behind a compound of thiophen with mercury and stearic acid (Ardagh and Furber, J.S.C.I. 1929, **48**, 73T).

Detection of Benzene and Homologues in Mixtures.—The use of dyes soluble in benzene and insoluble in other solvents has been suggested as a basis for a colorimetric method of determining benzene in mixtures. The dyes recommended by Formánek and coworkers (Chem.-Ztg. 1928, **52**, 325, and Chem. Obzor. 1928, **3**, 4) are Algol Red (BTK), B, 2G, or 5G, Lake Red Ciba B, Indanthrene Dark Blue BT, and Violet RT.

Weber (Chem.-Ztg. 1931, **55**, 201) uses the colour reactions given by polynitro-derivatives of benzene and its homologues with alkalis and certain higher alcohols for the purposes of detecting the hydrocarbons in the presence of each other or of other solvents. The test sample is nitrated, treated with the alcohol, and then with an excess of 2*N*-sodium hydroxide. The following colour reactions are specified :

Hydrocarbon.	Alcohol used.	Colour after treatment with sodium hydroxide.
Toluene	Benzyl alcohol	Reddish brown
m-Xylene	*cyclo*Hexanol	Intense green
Benzene	*iso*Amyl acetate followed by solid sodium hydroxide and acetone	Blue or violet

Stock (Farben-Ztg. 1930, **35**, 897) estimates benzene in mixtures by means of an insoluble compound which it forms with nickel cyanide and ammonia.

A method for estimating benzene in air is described by Dietrich (Chem. Fabr. 1932, **5**, 11): 25 litres of air are slowly aspirated through two columns each containing 25 c.c. of alcohol, which is then transferred to a measuring cylinder. 20 c.c. of a solution of 0·02 c.c. 40% $HCHO$ in 60 c.c. of pure H_2SO_4 is then carefully introduced, forming a lower layer. A brown ring forms at the liquid-liquid interface within 15 minutes if benzene is present even in concentrations as low as 0·01%. By titrating the residual formalin the amount of benzene withdrawn from the air can be estimated.

A colorimetric method of estimation has been evolved by Gavrilov (J. Chem. Ind. Russ. 1931, **8**, Nos. 23–24, 26–29). Air is passed through a 4 : 1 mixture of H_2SO_4 and fuming HNO_3 whereby $PhNO_2$ is formed. The mixture is cautiously diluted and made slightly alkaline with NH_4OH aq., extracted with ether and the $PhNO_2$ reduced to $PhNH_2$ by treating the ethereal solution with H_2SO_4 and Zn dust. After neutralisation with Na_2CO_3 an excess of tartaric acid and bleaching powder solution is added until a permanent rose-violet colour results. The colours produced are compared with those produced similarly from known quantities of benzene. The method may be modified for the estimation of benzene in petrol. A similar colorimetric method has been devised by Peronnet and Truhaut (Bull. Soc. Chim. 1933 [iv], **53**, 1464).

Standard tests for benzole are published by the National Benzole Association in " Standard Specifications for Benzole and Allied Products," 1929. E. V. E.

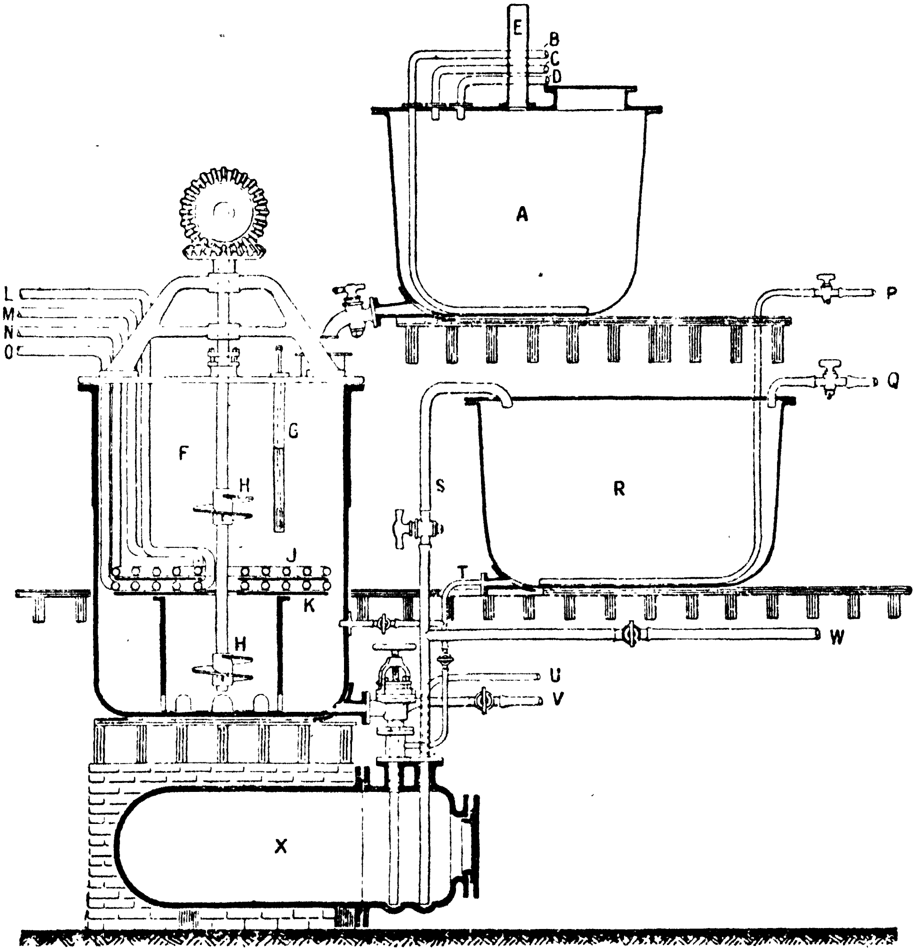
DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.

Nitro Derivatives.—*Nitrobenzene*, which is used mainly for the manufacture of aniline, is prepared by nitrating benzene under carefully controlled conditions with a mixture of nitric and sulphuric acids. The nitrator (fig. 1) consists of a cast-iron pan of capacity up to 1,600 gallons, fitted with a propeller type agitator and internal cooling coils made of pure chemical lead. There is also a thermometer pocket, the necessary inlets for materials and a tap at the bottom for running off the charge after nitration is complete.

The mixed acid used has the approximate composition : nitric acid 40%, sulphuric acid 53%, water 7%, and is usually made up separately and stored in large tanks ready for use. Waste acid from previous nitrations is also made use of : this contains approximately 72% sulphuric acid and no nitric acid. The general procedure is as follows.

The charge of waste acid (2,000 lb.) is blown into the nitrator, followed by the charge of benzene (2,600 lb.), and the temperature is adjusted to 24°C. by means of cooling water in the coils. With cooling water flowing, the mixed acid (approx. 5,300 lb., *i.e.* 1·01 times the theoretical quantity of nitric acid) is slowly run in at such a rate that the temperature does not exceed 26°C. When about four-fifths of the mixed acid has been run in, the rate of addition is increased so that the temperature reaches about 60°C. Agitation is continued for several hours in order to complete the reaction, when the charge is either blown to separating tanks or allowed to separate in the nitrator. The density of the nitrobenzene (1·235) is used as a guide to test whether or not nitration is complete. The nitric acid content of the aqueous layer is also a valuable control test ; it should be less than 1%. The process of settling takes at least 4–5 hours, after which the lower aqueous layer of waste acid is run off and passed to storage tanks.

The crude nitrobenzene is now passed on to the washing tanks. These are lead-lined vessels in which the agitation is conducted by blowing air through the liquids. The crude nitrobenzene is charged into the washer together with an amount of dilute alkali which experience shows is sufficient to neutralise the acid present. The contents of the washer are agitated thoroughly, and after settling, the neutral nitrobenzene is run to storage. It is frequently the practice to give two washes, the first with water alone (to remove the bulk of the acid) and the second with dilute caustic soda. The yield is 98% of the theoretical.



A, Mixed-acid pan.
B, Compressed-air pipe.
C, Sulphuric acid inlet.
D, Nitric acid inlet.
E, Acid-vapour pipe.
F, Nitrobenzene pan.
G, Thermometer.
H, Propeller agitator.
J, Lead cooling-coils.
K, Supporting grids.
L, M, } Cooling-water outlets.
N, O, } Cooling-water inlets.
P, Compressed-air pipe.
Q, Water inlet.
R, Nitrobenzene washpan.
S, Pipe from egg.
T, Nitrobenzene pipe.
U, Compressed-air pipe.
V, Waste-acid pipe.
W, Pipe to N. B. tank.
X, Air-pressure egg.

FIG. 1.

The nitrobenzene thus obtained is sufficiently pure for most purposes, but when it is required for perfumery (" Oil of Myrbane ") it is purified by vacuum distillation. If thiophen was present in the original benzene, this becomes converted to the dinitro-compound, the presence of which is detected by the red colour produced on shaking a sample of the contaminated nitrobenzene with alcoholic alkali.

Toluene.—The nitration of toluene is conducted in exactly the same manner as the nitration of benzene, but as three isomeric compounds are produced, it is necessary to effect a separation. Using mixed acid, the proportion of isomers obtained is : *ortho* 63%, *meta* 2%, *para* 35% ; but if pure nitric acid is used alone, the proportion of *ortho* is decreased slightly in favour of *para*. The separation of *ortho*- and *para*-nitrotoluenes is conducted by a combined process of fractional distillation and freezing. The first fraction (approx. 40%) consists of almost pure *ortho* ; it is further purified by redistillation. Pure *o*-nitrotoluene has b.p. 220°C. and exists in two modifications. The stable form has m.p. approx. −4°C. and the labile form at approx. −10°C. The residue after removal of the *ortho*-isomer is allowed to cool, when the *para* compound crystallises out and is separated from the oil by centrifuging. Pure *p*-nitrotoluene has m.p. 54·5°C. and b.p. 238°C. A good commercial sample should have a crystallising point of not less than 50°C. For estimation of *o*- and *p*-nitrotoluenes in mixtures, *see* Holleman, Rec. trav. chim. 1909, **28**, 408 ; 1913, **33**, 1 ; Ingold, J.C.S. 1931, 1959.

Nitroxylene is manufactured by the same process as its lower homologues, but as the reaction is even more complicated than with toluene, more rigid control is necessary. Xylene contains three isomers, and a mixture of five isomeric nitroxylenes is obtained. These are not separated but are reduced direct to xylidines, from which mixture it is possible to separate two isomers, *m*-xylidine (1 : 3 : 4) and *p*-xylidine (1 : 4 : 2), in a fairly high state of purity.

Schaarschmidt (Ber. 1924, **57**, 2065) describes the nitration of benzene by means of nitrogen peroxide in the presence of aluminium chloride, while Tronov and Sibgatullin (A. 1931, 610) use ethyl nitrate in the presence of the same catalyst. U.S.P. 1380186 describes a process for the nitration of benzene in the presence of mercury compounds ; this gives rise to nitro- and polynitro-phenols (*see also* Zakharof, A. 1929, 152 ; A. 1930, 1176 ; A. 1932, 51).

Dinitro-Derivatives.—When nitrobenzene is further nitrated the product consists of 91–93% *m*-dinitrobenzene (Holleman, Ber. 1906, **39**, 1715) together with small proportions of the isomers. *m*-Dinitrobenzene is usually prepared by the nitration of nitrobenzene rather than by the direct dinitration of benzene. Nitration is conducted as in the case of nitrobenzene manufacture in cast iron pans, but the conditions are more drastic than in the nitration of benzene. The mixed acid used contains a higher proportion of sulphuric acid and a higher temperature (115°C.) is employed to complete the reaction. When nitration is complete, as indicated by the composition of the waste acid and by the fact that a sample of the dinitro-compound solidifies on cooling, the agitation is stopped. After settling in the nitrator, the lower layer of acid is run off (70°C.) and the crude dinitro-compound is run into hot water. This is agitated in order to wash out acid, after which a wash with dilute alkali completes the neutralisation of the product. Owing to the solubility of the dinitro-compound in hot water, the wash liquors are preserved and used to wash a second batch. The crude product thus obtained has m.p. 86°–87°C. and should be a hard, non-greasy, crystalline material containing no nitrobenzene. Pure *m*-dinitrobenzene, which can be obtained by crystallising the crude material from benzene, has m.p. 89·8°C. The *o*-isomer has m.p. 118°C. and the *p*-isomer m.p. 172°C.

Dinitrotoluene is obtained by nitration of mixed nitrotoluene (*see* above) under the same conditions as used for the manufacture of dinitrobenzene. The principal product is 2 : 4-dinitrotoluene, but small quantities of the 2 : 6- and 2 : 3- are also formed. These are contained in the oily drainings from the crude crystallised product, and the purification of the crude material can be effected by centrifuging. Pure 2 : 4-dinitrotoluene has m.p. 71°C. and a good commercial sample should have a crystallising point not lower than 66·5°C. The preparation of *dinitroxylene* follows similar lines.

Trinitro - Derivatives. —*s* - *Trinitrobenzene* may be obtained by nitration of *m*-dinitrobenzene using a mixture of nitrosyl sulphate and nitric acid (E.P. 102216). The manufacture of trinitrotoluene is described under EXPLOSIVES.

Chloro-Derivatives.—*Benzene.* The chlorination of benzene is conducted in the presence of a suitable catalyst and many different materials have been proposed for this purpose. Iron is commonly used commercially. If chlorine is passed into benzene in the presence of iron, the main product is chlorobenzene, but during the later stages of the reaction there occurs some dichlorination with formation of *o*- and *p*-dichlorobenzenes. Depending on the requirements, the process is conducted on one of two lines ; if no dichlorobenzenes are required, the benzene is treated with about 60% of the theoretical amount of chlorine and the resulting mixture of benzene and chlorobenzene fractionated. If it is desired to chlorinate fully then the benzene is re-treated with approximately its own weight of chlorine and the resulting mixture separated by fractional distillation.

The reaction may be conducted in a jacketed iron vessel fitted with an agitator and a reflux condenser. The vessel is charged with dry benzene and the liquid is agitated with about 0·6–1·0% of its weight of iron borings and heated to the desired temperature. Where complete chlorination is required this is usually about 80°C. but when only chlorobenzene is being made, a lower temperature is employed. The reaction is exothermic and cooling water is used to control the temperature. The hydrogen chloride evolved passes up towers down which trickles a stream of water, and dilute hydrochloric acid thus forms a valuable by-product. After reaction, the contents of the vessel are neutralised and then distilled. In the complete chlorination, about 80% of chlorobenzene is obtained in the main fraction. The higher fraction consists of a mixture of *p*-dichlorobenzene (10–15%) and *o*-dichlorobenzene (1–3%) from which the *p*-isomer crystallises on cooling. Chlorobenzene has b.p. 132°, *p*-dichlorobenzene b.p. 174°, m.p. 53°, and *o*-dichlorobenzene b.p. 179°. For a description of various forms of plant used in the chlorination of benzene, *see* Cain, " Manufacture of Intermediate Products for Dyes," Macmillan, 1918, 7. B.P. 388818 describes a process for the chlorination of benzene in the vapour phase. Chlorobenzene is used in the manufacture of aniline by the amidation process and also for the preparation of nitro- and dinitrochlorobenzenes.

Toluene.—The chlorination of toluene on the technical scale presents problems which do not occur in the case of benzene. Substitution may occur either in the nucleus or in the side-chain ;

chlorination in the nucleus is favoured by the presence of metallic catalysts such as metallic chlorides, while side-chain substitution is favoured by high temperature and by light. For derivatives chlorinated in the side chain, special plant must be used. It is customary to employ either enamelled or tile-lined vessels or vessels lined with pure lead, and to heat by means of pure leaden steam-coils. Quartz mercury lamps hung in the interior have been used to accelerate the reaction. The extent of chlorination depends on which of the three products it is desired to obtain : benzyl chloride, benzal chloride, or benzotrichloride. If benzyl chloride is required, the charge of toluene is heated to boiling and chlorine passed in until the theoretical increase of weight has occurred. Phosphorus trichloride is sometimes used as a catalyst. As in the case of chlorobenzene manufacture, the hydrogen chloride is absorbed in water. The crude product is now washed with very dilute alkali and fractionated. Some unchanged toluene comes over first, followed by the main fraction of benzyl chloride (b.p. 179°), and later some higher chlorination products. The patent literature contains numerous references to special plant and processes for the chlorination of toluene. For a description of some of these, *see* Cain, " Manufacture of Intermediate Products for Dyes," Macmillan, 1918, p. 16. Mention may be made of the process of G.P. 139552, where sulphuryl chloride is the chlorination agent and benzal chloride is the product.

When benzal chloride and benzotrichloride are required, the chlorination is allowed to proceed further. The density of the liquid is used as a guide and chlorine is passed in until the density is above that of pure benzal chloride (d^{14} 1·2557). The amount of chlorine required is just below 2½ molecular proportions. It is not usual to separate the crude product at this stage, it is hydrolysed to a mixture of benzaldehyde and benzoic acid. Benzal chloride has b.p. 207°C.

Benzyl chloride is used for benzylating secondary amines for use as dyestuffs intermediates.

Oxidation.—*Benzene.* Catalytic oxidation of benzene by means of air at 400°–430° in the presence of vanadium pentoxide is stated to give 14–17% yields of maleic acid, together with maleic anhydride, quinone, and carbon dioxide (A. 1933, 1152 ; *see also* U.S.P. 1374740).

Toluene.—A fairly vigorous oxidation of toluene leads to benzoic acid, but under carefully controlled conditions, and using suitable reagents, it is possible to obtain benzaldehyde. Thus B.P. 331525, 331535 claim the use of a mixture of iron and vanadium oxides as catalysts for the aerial oxidation of toluene to benzaldehyde and benzoic acid. Manganese dioxide is used to convert toluene to benzaldehyde (B. 1930, 980). Weiss and Downs (Ind. Eng. Chem. 1920, **12**, 228) give an historical review of work on the catalytic oxidation of benzene and toluene. The following references are also of interest: Downs, J.S.C.I. 1926, **45**, 188T ; Maxted, *ibid.* 1928, **47**, 101T ; B.P. 298142 ; D.R.P. 101221, 107722, 158609, 174238, 175295 ; U.S.P. 1560297, 1589632, 1694122 ; Amer. Chem. Abstr. 1926, 339; 1929, 3680. W. A. S.

Benzene Sulphonic Acids.—*Benzene sulphonic acid,* $C_6H_5{\cdot}SO_3H$, may be prepared by treating benzene with concentrated sulphuric acid ; by oxidising benzene sulphinic acid ; by boiling *p*-diazobenzene sulphonic acid with alcohol.

On the large scale it is made as an intermediate for the manufacture of phenol. It has been found that in the usual method of treating benzene with an excess of concentrated sulphuric acid, as soon as the acid becomes diluted to 64% strength, the reaction stops. Hence there is always an excess of unreacted sulphuric acid. Guyot (Chim. et Ind. 1919, **2**, 879 ; B.P. 101973, 126039) found, however, that if benzene vapour is passed into 50–60% sulphuric acid, it is dehydrated to 64–66% when reaction occurs. This then continues until all the sulphuric acid is used up, on cooling pure benzene sulphonic acid crystallises out. Guyot (*l.c.*) describes a plant for continuous operation in which the benzene is separated from the water, washed with alkali, dried, and returned to the still.

The free acid can also be obtained from the lead or barium salt by decomposing with the calculated quantity of sulphuric acid ; it forms small deliquescent plates, containing 1·5 mol. H_2O.

Benzene sulphonyl chloride, $C_6H_5{\cdot}SO_2Cl$, m.p. 14°, made by the action of phosphorus pentachloride on the sodium salt, is not decomposed by cold water, and is of considerable value in the separation and identification of amines, and hydroxylic compounds, the corresponding sulphonamides and sulphonic esters, are usually well defined crystalline compounds.

Benzene m-*disulphonic acid,* $C_6H_4(SO_3H_2)$, obtained by the further action of sulphuric acid on benzene, or on the preceding compound, at 240°–250°. Under the influence of catalysts (mercury, ferrous sulphate), the *p*-isomeride is formed in addition (Lauer, J. pr. Chem. 1933 [ii], **138**, 81). Lamberts (D.R.P. 113784) employs *sodium hydrogen disulphate,* $NaH_3(SO_4)_2$ (obtained by heating sodium bisulphate with sulphuric acid), as a sulphonating agent at 200°. The free acid forms highly deliquescent crystals containing 2·5 mol. H_2O.

Benzene 1 : 3 : 5-*trisulphonic acid,*

$$C_6H_3(SO_3H)_3,$$

prepared by heating an alkali metal salt of the mono- or the *m*-di-sulphonic acid with sulphuric acid, until the sulphuric acid volatilises.

BENZIDINE. 4 : 4′-diaminodiphenyl.

BENZIL. Dibenzyl, $PhCO{\cdot}COPh$.

BENZINOFORM. Syn. for carbon tetrachloride.

BENZOFLAVINE *v.* ACRIDINE DYESTUFFS.

BENZOCAINE *v.* ANÆSTHESIN. Anæsthesine. Ethyl *p*-aminobenzoate, m.p. 90°–91°. Local anæsthetic.

BENZOIC ACID, $C_6H_5{\cdot}CO_2H$. Blaise de Viguere, in his " Traité du feu et du sel," published in 1608, described the preparation of benzoic acid by sublimation from gum benzoïn. Later, Scheele in 1775 extracted the acid from the gum as its calcium salt, by boiling with lime, and after concentrating the solution, acidifying with hydrochloric acid. Scheele also in 1785 obtained benzoic acid from cow's urine ; but it was not until 1829 that Liebig showed that the active substance present in the urine was hippuric acid, from the decomposition of which the benzoic acid is formed.

Occurrence.—Benzoic acid occurs in gum benzoïn, tolu balsam, storax, and various other natural resins ; in oil of bergamot and oil of cinnamon, in vanilla, calamus root, and ripe cloves; in various sweet-smelling flowers—thus in the flowers of *Unona odoratissima*, from which the perfume *ylang-ylang* is prepared. It occurs as hippuric acid, benzoylamino-acetic acid, in the urine of herbivora ; and in *castoreum*, a viscid, fœtid secretion, found in pouches situated in the perinæum of the beaver.

Formation.—By the oxidation of all compounds, containing a phenyl group with a single lateral side chain, such as toluene, benzaldehyde, cinnamic acid, etc. By the hydrolysis of benzotrichloride, $C_6H_5{\cdot}CCl_3$, with water, by heating benzonitrile, $C_6H_5{\cdot}CN$, with acids or alkalis. By passing carbon dioxide into benzene containing aluminium chloride:

$$C_6H_6 + CO_2 \rightarrow C_6H_5{\cdot}CO_2H.$$

Preparation.—(1) *From gum benzoin.* By sublimation : the gum, broken into small pieces, is introduced by means of a metal drawer into a closed vessel heated from below ; the vapour of the subliming acid passes into a side chamber, and condenses in a series of metal drawers, which can be removed at the end of the operation (Starting, Arch. Pharm. 1889, **227**, 410 ; 1893, **231**, 342). The yield is about 25% of the gum employed. A trace of an aromatic oil from the gum adheres to the crystals, imparting to them a pleasant odour of vanilla, and enhancing their value as a pharmaceutical preparation.

On a laboratory scale, the acid can be sublimed through a filter paper and collected inside a paper cone secured to the top of the vessel. (Mohr, Annalen, 1839, **29**, 177).

Scheele's method of extraction with slaked lime and water may also be used.

Wohler's method (Annalen, 1844, **49**, 245) consists in esterification with alcohol and hydrochloric acid of the benzoic acid in the gum, and removing the ester by steam distillation. Subsequently the ethyl benzoate is saponified with alkali, and the benzoic acid precipitated by acidification with hydrochloric acid.

(2) *From urine.*—The fresh urine is evaporated to one-third of its bulk, filtered, mixed with hydrochloric acid and allowed to cool. Hippuric acid crystallises out, and by boiling with concentrated hydrochloric acid, is hydrolysed into benzoic acid and glycocoll hydrochloride. In order to avoid the evaporation and the attendant disagreeable smell, the urine of the cow or horse may be allowed to putrefy, thereby inducing hydrolysis of the hippuric acid. The benzoic acid is then isolated by means of its insoluble ferric salt. The acid thus prepared smells of urine, and cannot be used in medicine.

(3) *From toluene.*—Most of the benzoic acid at the present day is manufactured from toluene (*v. infra*). It may be oxidised directly; or first chlorinated to benzyl chloride, which is subjected to hydrolysis and oxidation in one operation; or to benzotrichloride, which is hydrolysed directly to benzoic acid.

Direct oxidation, which avoids the formation of chloro derivatives, may be accomplished by heating with 40% nitric acid, preferably under pressure (U.S.P. 1332028, 1576999 ; D.R.PP. 101222, 107722) ; by manganese dioxide and sulphuric acid (E.P. 143392 ; D.R.PP. 175295, 21609) ; by aqueous chromic acid at 85° (U.S.P. 1458491) ; and also in the vapour phase, by using previously fused vanadium pentoxide as a catalyst at 300°.

Hydrolysis and oxidation of benzyl chloride with nitric acid is unsuited for preparing the acid on a manufacturing scale; it is more readily prepared by hydrolysing benzotrichloride by heating it with water under pressure:

$$C_6H_5{\cdot}CCl_3 + 2H_2O = C_6H_5{\cdot}CO_2H + 3HCl$$

by heating with milk of lime, or with caustic soda mixed with whiting or other insoluble material, the presence of which aids the reaction by preventing the benzotrichloride from forming a separate layer and also by promoting local superheating (D.R.PP. 47187, 82927, 85493). Hydrolysis can also be accomplished in the presence of zinc chloride by water (U.S.P. 1557153), or by acetic acid, in which case acetyl chloride is distilled off, the residue extracted with sodium carbonate, and the benzoic acid precipitated with hydrochloric acid:

$$\begin{aligned}&C_6H_5{\cdot}CCl_3 + 2CH_3{\cdot}CO_2H\\&\qquad = C_6H_5{\cdot}CO_2H + 2CH_3{\cdot}COCl + HCl\end{aligned}$$

Much of the benzoic acid used is obtained as a by-product in the manufacture of benzaldehyde by heating benzal chloride with milk of lime (*v.* BENZALDEHYDE). It can also be obtained by direct vapour phase oxidation of benzaldehyde in the presence of a catalyst such as nickel carbonate (F.P. 586383). The benzoic acid manufactured by these chlorination processes is always contaminated with chlorobenzoic acids, caused by nuclear chlorination.

(4) *From coal-tar oil.*—The creosote oil fraction (b.p. 160°–240°) obtained from coal tar, contains benzonitrile. Phenols are removed by washing with caustic soda (sp.gr. 1·1), and the remaining oil placed in a jacketed vessel, provided with an agitator and connected with a condenser and receiver. Caustic soda (sp.gr. 1·4) is added in excess, and wet steam passed in for some hours, as long as ammonia is evolved in quantity. The lower alkaline layer in the still is run off, neutralised with mineral acid, separated from traces of phenols and resinous matters, and while hot decomposed by the addition of excess acid. On cooling, pure benzoic acid separates in white crystals (E.P. 7867 ; D.R.P. 109122).

(5) *From phthalic acid.*—The phthalic acid is itself made by catalytic oxidation of naphthalene and its derivatives (*v.* PHTHALIC ACID). Molten phthalic anhydride at 210°–285° is treated with steam in the presence of a decarboxylating

agent, such as chromium or sodium phthalate; at intervals the benzoic acid is distilled off below 190° by steam (Monsanto Chem. Works, B.P. 341902; U.S.P. 1645180). Also by heating hydrogen phthalates at 200° with heavy metal catalysts, such as copper sulphate (E. I. Du Pont De Nemours & Co., U.S.P. 1712753). Impurities in the benzoic acid prepared by this method are naphthoquinone and phthalic acid; the former is removed by shaking a solution in benzene with aqueous sodium bisulphite; the latter by partial neutralisation with a non-volatile base and distilling out the benzoic acid with steam (I.G. Farbenind. A.-G., B.P. 329375).

(6) *From benzene.*—It can be prepared directly from benzene utilising the Friedel-Craft reaction, the benzene being added to carbon disulphide containing carbonyl chloride and aluminium chloride at 0° (U.S.P. 1542264); or by heating benzene with cyanuric chloride and aluminium chloride (Amer. Cyanamid. Co., U.S.P. 1734029).

Properties.—Benzoic acid crystallises in lustrous leaflets, m.p. 121·4°, d_4^{15} 1·2659, b.p. 249°; it is volatile even at 100°, so that it may be readily sublimed, and is sparingly volatile in steam, two litres of distillate contain 1 g. of the acid. It is readily soluble in alcohol and ether.

The calculated thermodynamic dissociation constant for benzoic acid is $6{\cdot}312 \times 10^{-5}$ (Brockman and Kilpatrick, J. Amer. Chem. Soc. 1934, **56**, 1483).

For absorption spectra, *see* Hartley and Headley, J.C.S. 1907, **91**, 319.

Gram mol. heat of combustion C_v 774·1 kg.-cal., C_p 771·7 kg.-cal.

Reactions.—When heated with lime, benzoic acid yields benzene (Mitscherlich). It is very stable towards oxidising agents; dilute chromic acid is without action on it, but by warming it with manganese dioxide and sulphuric acid it is converted into formic acid, carbon dioxide and phthalic acid (Carius, Annalen, 1868, **148**, 72). Reduction with sodium amalgam gives a mixture of benzyl alcohol, benzaldehyde and tetrahydrobenzoic acid (Aschan, Ber. 1891, **24**, 1864). Electrolytic reduction gives benzyl alcohol in good yield (Decans and Dufour, Bull. Soc. chim. 1925 [iv], **37**, 1167). With hydrogen and a platinum catalyst, Willstätter (Ber. 1912, **41**, 1479) obtained hexahydrobenzoic acid. Calcium benzoate on distillation yields benzophenone, $C_6H_5{\cdot}CO{\cdot}C_6H_5$, together with small quantities of benzene and anthraquinone (Kekule, Ber. 1872, **5**, 908). Taken internally, benzoic acid is excreted as hippuric acid (Wöhler).

Its esters have considerable medicinal and solvent value. For its use as an acidimetric standard, *see* Morely (J. Amer. Chem. Soc. 1912, **34**, 1027). It is also used as a thermochemical standard.

Benzoic acid is a permitted food preservative in a limited number of cases, *e.g.* (1) not exceeding 2,000 p.p.m. in unfermented grape juice and non-alcoholic wine made from such juice; (2) not exceeding 120 p.p.m. in brewed ginger beer; (3) not exceeding 450 p.p.m. in coffee extract; (4) not exceeding 250 p.p.m. in pickles and sauces made from fruit or vegetables (Public Health Regulations, No. 577, 1927).

Detection in Foodstuffs.—G. W. Monier-Williams (Rep. Public Health and Medical Subjects, 1927, No. 39) has given an extensive survey of both the detection and estimation of benzoic acid in foodstuffs. It can be detected and estimated by nitration and reduction to diaminobenzoic acid, which gives a brownish-red coloration in alkaline solution (Mohler, Bull. Soc. chim. 1890 [iii], **3**, 414), by converting the acid into salicylic acid with hydrogen peroxide, and then adding ferric chloride (Nicholls, Analyst, 1928, **53**, 19; *see also* Ionescu-Matiu and Popesco, J. Pharm. Chim. 1931 [viii], **14**, 438). It is also estimated by extraction with ether, and subliming out of the crude acid extract (R. Fischer and Stauder, Z. Unters. Lebensm. 1931, **62**, 658; 1927, **53**, 383; Leather, Analyst, 1931, **56**, 299).

SALTS AND ESTERS OF BENZOIC ACID.—Benzoic acid is monobasic. Most of the salts are soluble both in water and in alcohol. *Potassium benzoate*, $C_7H_5O_2K,3H_2O$, efflorescent laminæ. *Sodium benzoate*, $C_7H_5O_2Na,H_2O$, efflorescent needles, used for inhalation in tuberculosis. *Ammonium benzoate*, $C_7H_5O_2{\cdot}NH_4$, rhombic crystals, also used in medicine. *Calcium benzoate*,

$$(C_7H_5O_2)_2Ca,3H_2O,$$

lustrous needles used in the preparation of benzophenone, other hydrates are known. *Basic ferric benzoate*, $(C_7H_5O_2)_3Fe,Fe(OH)_3$, formed by the addition of ferric chloride in the presence of ammonia to a benzoate. This reaction is used in the separation of benzoic acid, and also in separating iron from manganese. *Mercuric benzoate*, $(C_7H_5O_2)_2Hg$, small white odourless crystals, a powerful antiseptic, stated to be successfully employed in syphilitic and similar diseases.

The esters of benzoic acid are best obtained by saturating with hydrogen chloride a solution of benzoic acid in the alcohol, digesting the mixture on the water bath for some hours, precipitating the ester with water, and purifying by distillation. *Methyl benzoate*, $C_6H_5{\cdot}CO_2Me$, b.p. 198·6°; *ethyl benzoate*, $C_6H_5{\cdot}CO_2Et$, b.p. 211·8°; n-*propyl benzoate*, $C_6H_5{\cdot}CO_2Pr^{\alpha}$, b.p. 230·7°; iso-*propyl benzoate*, $C_6H_5{\cdot}CO_2Pr^{\beta}$, b.p. 218°–219° (Perkin, Chem. Soc. Trans. 1896, **69**, 1025).

Benzyl benzoate.—This ester forms the therapeutically active portion of Peru balsam. It is a colourless oil, b.p. 173°/9 mm. The synthetic ester has certain advantages over that from balsam for medicinal use, as it is free from colour and smell, is constant in composition, and does not cause the irritation sometimes occasioned by Peru balsam owing to the free acids present (E. Erdmann, Pharm. 1906, J. **65**, 387).

Substitution Derivatives of Benzoic Acid.—The *o*-, and *p*- halo-, and nitro- benzoic acids are readily prepared by the oxidation of the corresponding toluene derivatives. o-*Chlorobenzoic acid*, m.p. 140°. The chlorine atom in this acid is very easily replaceable (Ullmann, Annalen, 1907, **353**, 312). The *m*-acid has m.p. 150°, the *p*-acid 243°. *o-Nitrobenzoic acid* has m.p. 144°, and the *p*-acid, m.p. 238°. Nitration of benzoic acid yields almost exclusively the *m*-acid, m.p. 141°. It can also be obtained by oxidation of *m*-nitrobenzaldehyde with sodium hypochlorite (Badische Anilin u. Soda Fabrik, D.R.P. 211959). Further nitration leads to the symmetrical 3 : 5-*dinitrobenzoic acid*, m.p. 206°.

In recent years there has been a general tendency to employ the esters of this 3 : 5-dinitro derivative as a reagent for identifying the alcohols, particularly those of the aliphatic series, which afford well defined crystalline compounds with sharp melting points. The preparation of this valuable reagent in good yield can be carried out as follows:

Benzoic acid (100 g.) is dissolved in concentrated sulphuric acid (250 c.c., sp.gr. 1·84) by warming on the steam bath. The flask is then cooled in running water and fuming nitric acid (180 c.c.), *very slowly* run in with agitation. At first much heat is developed, and the addition (¾ hour) must accordingly be carried out with caution ; towards the end it may be more rapid. After standing at room temperature for about 12 hours the solution is poured into cold water (250 c.c.) and allowed to stand several hours in order that the separation of solid may be more complete. The precipitate is filtered, well drained at the pump, then on porous earthenware, and finally dried *in vacuo* over a dehydrating agent. This solid, which is a mixture of *m*-nitrobenzoic and 3 : 5-dinitrobenzoic acids, and melts below 100°, is dissolved in a mixture of concentrated sulphuric acid (120 c.c., sp.gr. 1·84) and fuming sulphuric acid (20%, 50 c.c.) by warming on the steam bath, and the flask then cooled, when the solid is precipitated in a finely divided form. Fuming nitric acid (150 c.c.) is then slowly added (15 minutes) and the flask heated on the steam bath, under a good draught. The suspended solid rapidly enters into solution, a vigorous action setting in with evolution of copious brown fumes, too violent reaction should be abated by cooling the flask in water. The flask is then heated on the steam bath for about 12 hours when a heavy copious crystalline precipitate is formed. The mixture is cooled, poured into cold water (500 c.c.), and the crystalline precipitate filtered off, pressed, and washed with successive small quantities of ice-cold water (*c.* 400 c.c.). The product is pure 3 : 5-dinitrobenzoic acid, in hard, white, lustrous, cubic crystals, m.p. 204°–206°, and the yield is invariably 85–90 g.

For the identification of alcohols the 3 : 5-dinitrobenzoic acid is converted by warming with phosphorus pentachloride into the acid chloride. The pure alcohol is condensed with the acid chloride in pyridine solution ; if, however, only an aqueous solution of the alcohol is available, it is condensed with the acid chloride in alkaline solution to give the corresponding ester. The alkyl 3 : 5-dinitrobenzoates are all well-defined crystalline compounds, and the melting-point and a mixed melting-point with an authentic specimen, serves as proof of the identity of an alcohol. The following are the melting-points of the esters of the commoner alcohols :

Methyl	3 : 5-dinitrobenzoate,	m.p. 110°.
Ethyl	,,	m.p. 93°.
n-Propyl	,,	m.p. 74°.
iso-Propyl	,,	m.p. 121°.
n-Butyl	,,	m.p. 61°.
iso-Butyl	,,	m.p. 87°.
tert-Butyl	,,	m.p. 141°.
Allyl	,,	m.p. 49°.
iso-Amyl	,,	m.p. 61°.

The advantages of 3 : 5-dinitrobenzoic acid for this purpose over such reagents as phenyl- or xenyl-carbimide are twofold. Firstly, the alcohol to be identified need not be anhydrous as is necessary with these other reagents ; and, secondly, owing to the high molecular weight of 3 : 5-dinitrobenzoic acid, a small amount of an alcohol will give a considerable quantity of an ester.

The symmetrical 2 : 4 : 6-*trinitrobenzoic acid* has recently been suggested as a similar reagent for alcohols (Chang and Kao, J. Chinese Chem. Soc. 1935, **3**, 256).

Benzoic Anhydride, $(C_6H_5CO)_2O$. First prepared by Gerhardt (Ann. Chim. Phys. 1853 [iii], **37**, 299) by the action of benzoyl chloride on sodium benzoate or on sodium oxalate, or of phosphorus oxychloride on sodium benzoate.

Preparation.—Benzoic anhydride is best prepared by the slow distillation of a mixture of benzoic acid and acetic anhydride, in the presence of phosphoric acid. The residual benzoic anhydride is finally distilled in vacuum, and crystallised from a mixture of benzene and petroleum. For an adaptation of this to large-scale working, *see* "Organic Syntheses," 1923, III, 21.

$$C_6H_5{\cdot}CO_2H + (CH_3CO)_2O \rightarrow C_6H_5CO{\cdot}O{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO_2H$$

$$C_6H_5{\cdot}CO_2H + C_6H_5{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 \rightarrow (C_6H_5CO)_2O + CH_3{\cdot}CO_2H$$

Treatment of benzoyl chloride with sodium carbonate and pyridine gives a quantitative yield of the anhydride (Deninger, J. pr. Chem. 1894 [ii], **50**, 479 ; Minunni, Gazzetta, 1892, **22**, iii, 213). Commercially it is made by treating benzenesulphonyl chloride with sodium benzoate (Chem. Fab. von Heyden, D.R.P. 123052 ; Chem. Zentr. 1902 [ii], 518) ; by treating benzoic acid or sodium benzoate with methyl chlorsulphate (Badische Anilin u. Soda Fabrik, D.R.P. 146690 ; Chem. Zentr. 1904 [i], 65) ; by treating benzoic acid with acetic anhydride in benzene or xylene (Kaufmann and Luterbacher, Ber. 1909, **42**, 3483) ; by the action of concentrated sulphuric acid on benzotrichloride, or by the action of sulphuryl chloride on a mixture of sodium and calcium benzoates (D.R.P. 161882) ; and by heating a mixture of benzoic acid and benzoyl chloride in a stream of inert gas at 210°–230° (Monsanto Chem. Co., U.S.P. 1948342).

Properties.—Rhombic prisms, m.p. 43°, d_4^{15} 1·1989 at 15°/4°. Insoluble in water, readily soluble in both alcohol and ether.

Reactions.—Water decomposes it only slowly in the cold, but more rapidly on boiling. Towards ammonia, amino- and imino-compounds, alcohols and phenols, it behaves like benzoyl chloride (*q.v.*). For this reason it is used as a benzoylating agent, and it has the advantage over benzoyl chloride that no hydrogen chloride, a substance which has a very prejudicial effect on many organic compounds, is liberated during its action.

With sulphuric acid in carbon disulphide it gives an addition compound, $C_{14}H_{12}O_7S$, m.p. 72° (M. Bergmann and F. Radt, Ber. 1921, **54**, 1652). With diazomethane, it gives, besides methyl benzoate, diazoacetophenone (W. Bradley and R. Robinson, J. Amer. Chem. Soc. 1930, **52**, 1558).

Benzoyl Chloride, $C_6H_5{\cdot}COCl$. First obtained by Liebig and Wöhler, by passing chlorine into benzaldehyde (Ann. 1832, **3**, 262).

Preparation.—Benzoic acid is heated with a slight excess of phosphorus pentachloride (Cahours, Ann. Chim. Phys. 1848 [iii], **23**, 334), the resulting benzoyl chloride being freed from phosphoryl chloride by fractional distillation.

It is prepared from salts of benzoic acid, by treatment with sulphur dioxide and chlorine (Meister, Lucius, and Brüning, D.R.P. 210805), or with methylchlorsulphate or sodium chlorsulphonate (Badische Anilin u. Soda Fabrik, D.R.P. 146690) ; or by the action of sulphuryl chloride on benzoic acid. By addition of water to benzotrichloride containing zinc chloride in suspension at 100°–120°, benzoyl chloride can be obtained in 85% yield (Mathieson Alkali Works, U.S.P. 1557153).

Commercial benzoyl chloride is usually contaminated with chlorbenzoyl chloride and with traces of benzaldehyde.

Properties.—Colourless liquid, m.p. −1°, b.p. 197°, d_{15}^{15} 1·2187. It has a pungent odour and the vapour is lachrymatory.

Reactions.—Benzoyl chloride is hydrolysed with water slowly in the cold, but rapidly on heating. It readily reacts with compounds containing hydroxyl-, amino-, or iminio-groups, introducing benzoyl in place of hydrogen, and it is therefore employed as a test for the presence of these groups in a compound. Thus with *ammonia* it forms benzamide, $C_6H_5{\cdot}CONH_2$; with *alcohol* it yields ethyl benzoate ; with aniline, benzanilide and dibenzanilide. Benzoyl chloride readily chlorinates in the presence of ferric chloride, to give 85% *m*-chlorbenzoyl chloride, which is hydrolysed by water to *m*-chlorbenzoic acid (E. Hope and G. C. Riley, J.C.S. 1922, **121**, 2510).

With diazomethane it gives a nearly quantitative yield of diazoacetophenone (W. Bradley and R. Robinson, J.C.S. 1928, 1310). With sulphuric acid in chloroform it gives an addition complex, $C_7H_7O_5ClS$, m.p. 52° (M. Bergmann and F. Radt, Ber. 1921, **54**, 1652).

BENZOIN, $PhCH(OH){\cdot}COPh$, a keto-alcohol of dibenzyl (*v.* Acyloins).

BENZOIN *v.* Balsams.

BENZONAPHTHOL. Trade name for *β*-naphthyl benzoate, $C_6H_5{\cdot}CO{\cdot}O{\cdot}C_{10}H_7$, m.p. 107°–110°. Intestinal antiseptic.

BENZOPHENONE, $(C_6H_5)_2CO$, m.p. 48°–48·5°, b.p. 306°, d_{20}^{50} 1·097. This useful synthetic ketone, diphenyl ketone, is used in perfumery when geranium, new-mown hay and many perfumes of the heavy oriental type require rounding off. It should be free from the slightest trace of chlorine (*v.* Ketones).

E. J. P.

BENZOSALIN. Trade name for methyl benzoylsalicylate,

$$C_6H_4(O{\cdot}CO{\cdot}C_6H_5)COOCH_3,$$

m.p. 85°. Intestinal antiseptic.

BENZOSOL. Trade name for guaiacol benzoate, $C_6H_5{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$, m.p. 60°. Internal antiseptic.

BENZOTRICHLORIDE, $C_6H_5{\cdot}CCl_3$.

BENZYL ESTERS. Several of the fatty acid esters are used in synthetic perfumery, but not to a large extent. *Benzyl acetate*, $CH_3{\cdot}CO_2{\cdot}CH_2Ph$, sp.gr. 1·060, *n* 1·5030, has a good jasmin odour.

Benzyl benzoate, $PhCO_2{\cdot}CH_2Ph$, sp.gr. 1·120, m.p. 19°–20°, b.p. 320°, is used to a considerable extent, both as a fixative, and as a solvent for artificial musk, it has a slight balsamic odour. It should be chlorine-free. Benzyl benzoate and dibenzyl succinate,

$$PhCH_2O{\cdot}OC{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OCH_2Ph,$$

are antispasmodics. E. J. P.

BENZYLIDENE ACETONE,

$$C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH_3,$$

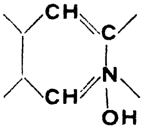
m.p. 39°–40°, b.p. 260°–262°, sp.gr. 1·0377. This synthetic perfume is essential in bouquets of the sweet-pea type, the odour of which it recalls in a marked degree. It is also used as an ingredient in numerous other perfumes, such as lilac, magnolia, new-mown hay and heather. It should be absolutely free from chlorine.

E. J. P.

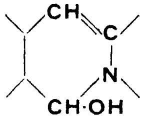
BERBAMINE *v.* Isquinoline Alkaloids.

BERBERINE, $C_{20}H_{19}O_5N$, is contained in various species of *Berberis*, especially *B. vulgaris* (Linn.) (the barberry), which also contains *berbamine*, $C_{36}H_{38}O_6N_2$ (Hesse, Ber. 1886, **19**, 3193) and *oxyacanthine* (*v. infra*), in *Hydrastis canadensis* (Linn.) together with hydrastine and canadine, in *Coptis Teeta* (Wall.), which contains as much as 8%, and in many other plants, but not in calumba root (Gordin, Arch. Pharm. 1902, **240**, 146).

Preparation.—The best available material from which to extract berberine is the root of *Hydrastis Canadensis* (Linn.) ("Golden Seal"), which contains about 4% of the alkaloid. The finely-powdered hydrastis root is exhausted with alcohol, the greater part of the alcohol removed by distillation, and the alkaloid converted into sulphate or nitrate by the addition of sufficient dilute sulphuric or nitric acid. The crude berberine salt which separates is collected, dissolved in water, and mixed with acetone and sodium hydroxide, when the crystalline condensation product, anhydroberberineacetone, separates (Gaze, Z. Naturwiss. Halle, 1890, **62**, 399). After recrystallisation, this product melts at 175° (corr.) (Pyman, J.C.S. 1911, **99**, 1690) ; it yields with hot dilute mineral acids the corresponding berberinium salts. On a large scale hydrastine may first be extracted from golden seal by benzene containing a trace of ammonia, and the berberine then extracted from the residue with dilute aqueous acetic acid. The alkaloid is isolated as the hydrochloride or sulphate, which may be purified by crystallisation (Schmidt, Amer. J. Pharm. 1919, **91**, 270). The free base exists in two isomeric forms, represented by the partial formulæ below:



I.



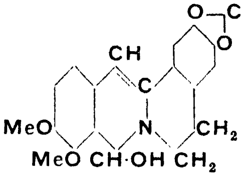
II.

as the quaternary ammonium hydroxide, berberinium hydroxide (I), which is known only in aqueous solution, and as the carbinolamine berberine (II), also termed berberinal and berberinol. For the nomenclature of berberine and its salts, *see* Perkin (J.C.S. 1918, **113**, 503). A solution of berberinium hydroxide is prepared by adding the equivalent quantity of barium hydroxide to an aqueous solution of berberinium sulphate, whilst the addition of an excess of sodium hydroxide to this solution affords a precipitate of the carbinolamine berberine, which is extracted by ether, and crystallises on concentrating the solution (Gadamer, Arch. Pharm. 1905, **243**, 31).

Properties.—Berberine, $C_{20}H_{19}O_5N$, crystallises from ether in yellow needles which melt at 144° and are anhydrous. It is insoluble in cold water, but on warming gradually yields a solution of berberinium hydroxide. It dissolves in acids, giving salts of berberinium hydroxide. The berberinium salts, $C_{20}H_{18}O_4NX$ (where X is a monobasic acid radical) crystallise well, and are of a yellow or red colour. They are sparingly soluble in water, especially in the presence of mineral acids or salts. Their aqueous solutions are neutral to litmus, optically inactive, and have a bitter taste. Berberine is not poisonous to man and is used medicinally, like preparations of the plants containing it, as a stomachic, in the treatment of diarrhœa and of the vomiting of pregnancy. Berberine sulphate has been used in the treatment of oriental sore. The pharmacological action has been described by Floriani (Anales farm. bioquim. 1931, **2**, 205) and by Chopra, Dikshit and Chowhan (Indian J. Med. Res. 1932, **19**, 1193).

Detection and Estimation.—Chlorine water gives with a solution of the hydroxide a bright red coloration even in very dilute solutions. The detection of berberine in plants is described by Gordin (Arch. Pharm. 1902, **240**, 146) and Mayrhofer (Pharm. Post. 1914, **47**, 547). For other microchemical reactions, *see* Wagenaar (Pharm. Weekblad, 1930, **67**, 77) and Ess (Schweiz. Apoth.-Ztg. 1918, **56**, 104). The alkaloid is estimated by precipitation as the sulphate in alcoholic solution, followed by decomposition with aqueous potassium iodide solution and titration of the resulting acid solution with N/10 sodium hydroxide. For the use of picrolonic acid as a reagent in the estimation and micro-chemical detection of berberine, alone or in the presence of hydrastine, *see* Richter (Arch. Pharm. 1914, **252**, 192), Wasicky and Joachimowitz (Arch. Pharm. 1917, **255**, 497), and Almgren (Svensk Farm. Tidskr. 1924, **28**, 377).

Constitution.—The main features of the constitution of berberine were determined by Perkin (J.C.S. 1889, **55**, 63; 1890, **57**, 992) by a study of its oxidation products, and subsequent work by Gadamer (Chem.-Ztg. 1902, **26**, 291, 385; Arch. Pharm. 1905, **243**, 31; 1910, **248**, 43), Perkin and Robinson (J.C.S. 1910, **97**, 321), and Tinkler (J.C.S. 1911, **99**, 1340) established the formula given below:



The earlier recorded synthesis of berberine by Pictet and Gams (Ber. 1911, **44**, 2480) could not be confirmed by Haworth, Perkin and Rankin (J.C.S. 1924, **125**, 1686), but syntheses of the alkaloid have been described by Perkin, Rây and Robinson (J.C.S. 1925, **127**, 740) and Haworth, Koepfli and Perkin (J.C.S. 1927, 548). Attention may be drawn to the similarity between the formula of berberine and that of hydrastine.

Oxyacanthine, which is now believed to have the formula $C_{36}H_{38}O_6N_2$, accompanies berberine in *Berberis vulgaris* (Linn.) (Polex, Arch. Pharm. 1836 [ii], **6**, 271; Hesse, Ber. 1886, **19**, 3190; Rüdel, Arch. Pharm. 1891, **229**, 631), and may be isolated from the mother-liquor from which all the berberine salt has crystallised, by precipitation with sodium carbonate. After purification by crystallisation of the hydrobromide or sulphate, regeneration and crystallisation from ether, it has m.p. 216°–217° (Späth and Kolbe, Ber. 1925, **58** [B], 2280). Its constitution has been discussed by Späth and Pikl (Ber. 1929, **62** [B], 2251), von Bruchhausen and Gericke (Arch. Pharm. 1931, **269**, 115) and by von Bruchhausen, Oberembt, and Feldhaus (Annalen, 1933, **507**, 144) (*see iso*Quinoline Alkaloids). F. L. P.

BERGAMOT, ESSENTIAL OIL OF.

The oil contained in the fresh peel of the fruit of *Citrus aurantium* Linn., subspecies *Bergamia*, N.O. Rutaceæ, cultivated principally in Southern Calabria. The oil is obtained by pressing the fruit in a machine which consists of a moving corrugated copper or zinc disc against a stationary one. The expressed oil is filtered by enclosing it in a cloth bag of fine texture held in the narrow neck of a tinned-copper receptacle in such a way that pressure can be exerted on the bag and its contents by means of weights. The residue, which contains some oil, is distilled for the production of an oil of inferior quality.

Characters.—Bergamot oil is a greenish or greenish-yellow liquid with a pleasant odour and a bitter, disagreeable taste. Sp.gr. 0·882–0·886, opt. rot. +12° to +24°, n_D^{20} 1·464–1·467. Ester content 36–40% calculated as linalyl acetate. Residue on evaporation 4–6%.

Constituents.—Octylene, camphene, *d*-limonene, bisabolene, linalol, linalyl acetate, nerol, terpineol, and bergaptene (*q.v.*) a crystalline non-volatile substance, m.p. 190°–191°. The saponification value of the non-volatile residue is 136–200.

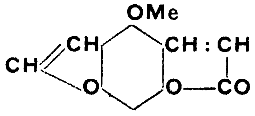
Adulterants.—The addition of terpenes lowers the ester value. Terpinyl acetate is detected by determining the ester value after 1 and 2 hours' saponification ; the difference between the two results should not be more than 0·5%. Glyceryl acetate is detected by shaking 10 c.c. of the oil in a separator with 10 c.c. of light petroleum, 2·5 c.c. of alcohol, and 20 c.c. of water, filtering the aqueous layer, neutralising with $\frac{N}{2}$ alcoholic potash solution, and saponifying for one hour with 10 c.c. of $\frac{N}{2}$ alcoholic potash. Not more than 0·2 c.c. should be absorbed. Certain artificial esters (*e.g.* ethyl phthalate) are detected by saponifying 1 g. of the oil with 3 c.c. of 10% solution of potash in absolute alcohol, under a reflux condenser for 1 minute and allowing to cool. No cloudiness or crystalline precipitate should be produced after 1 hour.

To detect ethyl citrate, 2 g. of the oil are saponified with alcoholic potash, the solution is diluted with water, neutralised with hydrochloric acid, the alcohol removed by evaporation, and the solution extracted with ether and filtered. The presence of citric acid is detected in the aqueous solution by Denegès' test.

Distilled oil of Bergamot has a specific gravity of about 0·870, ester content 4–7%, non-volatile residue 0·2%. Oil of Bergamotella, the unripe windfalls or bastard fruits, has sp.gr. 0·890–0·898, ester content 20–25%, residue on evaporation may be as high as 11%.

Bergamot oil is chiefly used in perfumery for the production of eau-de-cologne and for soap scenting. C. T. B.

BERGAPTENE. Separates as a crystalline magma from the essential oil of Bergamot on standing, and may be purified by sublimation. It crystallises in hard white needles from alcohol, m.p. 190°–191°, with partial sublimation, and is tasteless and odourless at the ordinary temperature. It is a coumarin derivative having the structural formula :



(Pomeranz, Monatsh. 1891, **12**, 379 ; *cf.* Karrer, Glattfelder, and Widmer, Helv. Chim. Acta, 1920, **3**, 541.)

BERGER PROCESS *v.* ALUMINIUM.

BERI-BERI *v.* B_1 VITAMIN.

BERTHIERITE *v.* ANTIMONY.

BERTRANDITE. A beryllium mineral (Be 15·1%) with the composition,

$$H_2Be_4Si_2O_9,$$

occurring as thin lozenge-shaped (orthorhombic) plates with a characteristic pearly lustre on the large surface. It has been found in sparing amounts in granite at several localities in Cornwall (Min. Mag. 1911, **16**, 47 ; 1913, **17**, 15), France, Bohemia and the United States, it is apparently an alteration product of beryl. L. J. S.

BERYL. A mineral consisting of beryllium and aluminium silicate approximating to $Be_3Al_2Si_6O_{18}$, and crystallising in the hexagonal system. The ancient name, βηρυλλος, included also some other gem-stones of a greenish colour. The crystals are usually quite simple in form, with only the hexagonal prism and basal plane ; the habit being commonly prismatic and the prism faces striated vertically. They are usually cloudy or opaque with a pale greenish or yellowish colour, and are sometimes of considerable size. In another, less common, type the crystals are tabular in habit with a large basal plane and a short prism, and differing also in colour, being colourless or pink. Beryl of this type is further distinguished by its content of alkalis, and it has been called alkali-beryl, caesium-beryl, vorobyevite (W. I. Vernadsky, 1908 ; with many different variations in spelling from the original Russian form воробьевитъ), rosterite (G. Grattarola, 1880) for pink crystals from Elba, and morganite for material of gem quality. The amounts of alkalis shown by different analyses range up to Li_2O 2%, Na_2O 4·22%, K_2O 2·25%, Cs_2O 4·56%, Rb_2O 1·34%. Further, all beryls contain H_2O 1–2%. No satisfactory general formula has yet been deduced for the mineral. W. I. Vernadsky (1908) expressed the composition by the formula $x BeAl_2Si_4O_{12} \cdot y A$, where A is BeH_2SiO_4, $BeSiO_3$(?), Cs_2SiO_3, Li_2SiO_3, or Na_2SiO_3. F. Zambonini and V. Caglioti (Gazzetta, 1928, **58**, 131) explain variations from the usually accepted formula $Be_3Al_2Si_6O_{18}$ by mixed crystals with R_2SiO_3 and $R_2Al_2Si_2O_8$, where R is Li_2, Na_2, K_2, Cs_2, and some Be, Ca, Mg. Corresponding with this variation in chemical composition, there is a wide range in the density of beryl from 2·545 to 2·910, and in the refractive indices ω 1·570–1·602, ϵ 1·564–1·595. The hardness is 7½–8, so that the mineral is well adapted to withstand wear as a gemstone. The mineral is not attacked by acids except hydrofluoric ; and before the blowpipe it is fusible only with difficulty on the edges.

Beryl usually occurs as single crystals as an accessory constituent of certain granite-pegmatites, or sometimes in mica-schists near the contact with these pegmatites. Alkali-beryl is found together with lepidolite and rubellite in lithia-pegmatites in the Urals, California and Madagascar. An unusual type of occurrence is that of the best quality of emeralds in a carbonaceous limestone of Cretaceous age in the Muzo district, Colombia, South America. The mineral is rather sporadic in its distribution and sparing in amount, and no large deposits have been found. The present sources of supply are mostly limited to hand-picked material obtained as a by-product in felspar quarries that have been opened up in pegmatite veins. In 1928 crystals up to 18 ft. in length and 4 ft. in diameter, and estimated to weigh 18 tons, were exposed in a felspar quarry at Albany in Maine, U.S.A., but crystals of this size are exceptional. In the Leydsdorp district in north-eastern Transvaal, where mining for emerald has been carried on in biotite-schist and hornblende-schist at a granite contact, a quantity of common beryl has been set aside as a by-product. In the granite-pegmatites near Jackals Water in the Steinkopf district, Cape Province, South Africa, crystals up to 3 ft. in length have been obtained. Occurrences have also been reported in pegmatites in South-West Africa. Crystals of beryl up to 8 in. across have been found in the lithia-bearing pegmatites of the Huron claim, Winnipeg River district in south-east Manitoba. The pegmatites in the Black Hills in South Dakota, U.S.A., have also yielded large crystals of beryl, and large crystals are occasionally found in the felspar quarries of the south of Norway. Other localities where good sized crystals of beryl are found are in the gem mines, also in pegmatites, in Madagascar, Brazil, and California. A list of beryl localities is given by M. Hosenfeld (Wiss. Veröff. Siemens-Konz. 1929, **8** [i], 21 ; B. 1929, 722), and in "Beryllium (Glucinum) and Beryl," The Mineral Industry of the British Empire and Foreign Countries, Imperial Institute, London, 1931.

Beryl is the only mineral that is found in sufficient quantity for use in the extraction of beryllium and in the preparation of its little-used salts. It, however, contains only about 5% Be, and the few other minerals containing a larger amount are of quite rare occurrence ; these are : bromellite 36·0, hambergite 19·2, phenakite 16·4, bertrandite 15·1, swedenborgite 12·3, chrysoberyl 7·1, beryllonite 7·1, euclase 6·2, trimerite 6·0, barylite 5·6, herderite 5·5, rhodizite 5·2% Be. All these are found in pegmatites, and it is in such rocks that a concentration of the element beryllium occurs. Pegmatites are considered to represent the residual mother-liquor after the main crystallisation of igneous magmas, which has been squeezed out along rock fissures. The concentration of beryllium in this residium is thought by V. M. Goldschmidt to be due to the small size of the beryllium atom (radius of 0·34Å.), which enables it to escape through the crystal lattices of the more common rock-forming minerals.

As yet the main use of beryl is as a gem-stone. The clear grass-green variety is the *emerald*, one of the most valuable of gems on account of the rarity of flawless material. Gem-stones of a greenish, bluish, or sea-green colour are known as *aquamarine*. Pink beryl of gem quality has been called *morganite*, and a golden beryl from South-West Africa is given the name *heliodor*. For a description of gem material and its occurrences, *see* M. Bauer, "Precious Stones," transl. by L. J. Spencer, London, 1904 ; 3rd German ed., "Edelsteinkunde," by K. Schlossmacher, Leipzig, 1928–32. On the gem beryls from Madagascar, *see* A. Lacroix, "Minéralogie de Madagascar," Paris, 1922, **1**, 545 ; **2**, 88 ; 1923, **3**, 296. L. J. S.

BERYLLIUM *v.* GLUCINUM.

BERYLLONITE. Beryllium sodium phosphate, $BeNaPO_4$, containing Be 7·1%, found as orthorhombic crystals in pegmatite at Stoneham in Maine, U.S.A., and more recently also at Newry in Maine (C. Palache and E. V. Shannon, Amer. Min. 1928, **13**, 392 ; H. J. Fraser, *ibid.* 1930, **15**, 361). The patterns of X-ray photographs, however, suggest that the crystals are really monoclinic (B. Gossner and J. Besslein, Centr. Min. A, 1934, 144). Sp.gr. 2·85, hardness 5½–6. Clear colourless crystals have occasionally been cut as gem-stones. L. J. S.

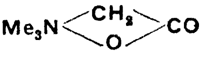
BERZELIANITE. Native copper selenide, Cu_2Se, occurring in a black powdery form in calcite at Skrikerum in Sweden and at Lehrbach in the Harz. Named after the Swedish chemist J. J. Berzelius (1779-1848), who first analysed it. A specimen of the Swedish mineral presented by him in 1817 is preserved in the British Museum collection of minerals. L. J. S.

BERZELIITE. Arsenate of calcium, manganese, and magnesium $(Ca,Mn,Mg)_3 As_2O_8$, occurring as small yellow cubic crystals, and as compact masses, with ores of iron and manganese at Långban in Wermland, Sweden. Also named after J. J. Berzelius. Other forms of the same name, berzeline and berzelite, have been applied to these, as well as to some other minerals. L. J. S.

BETAFITE. The betafite group of minerals recognised by A. Lacroix in 1912 in the pegmatites of Madagascar, includes betafite, samiresite, and blomstrandite (of G. Lindström, 1874). They are titano-columbates (and tantalates) of uranium, etc., crystallising in the cubic system, and closely allied to pyrochlore and hatchettolite. From the former they differ in containing only little lime and rare earths and an absence of alkalis and fluorine ; and from the latter in containing titanium. Betafite is a hydrated titano-columbate of uranium (UO_3 26–28%). Sharply developed octahedral crystals with the edges truncated by faces of the rhombic-dodecahedron have been found in considerable numbers at Ambolotara near Betafo, and other localities in Madagascar. They reach an inch in diameter, and show a dull yellow weathered surface, but in the interior the material is brownish-black with a bright greasy lustre. Sp.gr. 3·59–4·475 depending on the degree of hydration. Samiresite, a titano-columbate of uranium (UO_3 21%) and lead, is from Samiresy near Antsirabe. In blomstrandite a part of the columbium is replaced by tantalum. (A. Lacroix, "Minéralogie de la France et de ses colonies," 1913, vol. v ; Minéralogie de Madagascar, 1922, **1**, 378 ; **2**, 127.) Betafite has since been found near Lake Baikal in Siberia (G.P. Chernik, 1927). L. J. S.

BETAFORM. Bismuth tribromocatechol.

BETAINES are completely methylated amino-acids with quinquevalent nitrogen. Bases of this type derived from several of the amino-acids of protein occur naturally in plants and animals. *Betaine* par excellence



$$Me_3N\begin{matrix}\diagup CH_2 \diagdown\\ \diagdown\ O\ \diagup\end{matrix}CO$$

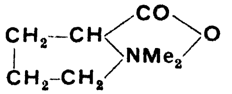
is the most important and the simplest, being trimethylglycine, and later gave its name to the whole class (for the nomenclature and general properties of which, *see* Willstätter, Ber. 1902, **35**, 584, and S. Komatsu, Mem. Coll. Sci. Kyoto, 1916, **1**, 369). Pfeiffer (Annalen, 1928,

465, 20) has isolated *cis-* and *trans-* forms of α-phenylcinnamic acid and concludes that betaines are dipolar and not internal ring compounds. Betaine (acetobetaine, oxyneurine, lycine) occurs in *Beta vulgaris*, the sugar-beet, and in all other *Chenopodiaceæ* examined, sporadically in a number of other plants, in mussels, cuttle fish, crayfish, etc. For localisation and migration of betaine in plants, *see* Staněk (Z. physiol. Chem. 1911, **72**, 402, and Z. Zuckerind. Böhm. 1916, **40**, 300). Young sugar beets contain more than older ones. Crude beet-sugar may contain 0·375% of betaine (Waller and Plimmer, Proc. Roy. Soc. 1903, **72**, 345). The only practical natural source is the final mother liquor left after desaccharification of the molasses by strontium, which liquor, with 20% of water, may contain 115 g. of betaine per kilo. The extraction of betaine is apparently best carried out by vigorous agitation with 96% alcohol. After evaporation of the alcohol the betaine is converted into chloride and crystallised as such. Yield of the liquor of pure chloride 10–12% of the liquor employed (Ehrlich, Ber. 1912, **45**, 2409 ; D.R.P. 157173 ; *cf.* Stoltzenberg, Ber. 1912, **45**, 2248; D.R.P. 243332 ; and Chem. Zentr. 1914 [i], 22 ; Urban, Z. Zuckerind. Böhm. 1913, **37**, 339 ; Andrlik, *ibid.* 1915, **39**, 387).

Betaine is also obtained by the oxidation of choline (" oxyneurine," Liebreich, 1869), by the methylation of glycine and, as chloride, by the action of trimethylamine on chloracetic acid. A synthesis by heating methyldimethylaminoacetate with methyl halides and subsequent hydrolysis of the betaine ester with acids is stated to give a quantitative yield, and has been patented (D.R.P. 269338). For the isolation from plant extracts (Schulze) and estimation (Staněk), *see* CHOLINE.

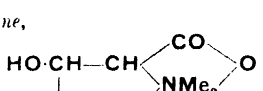
Betaine crystallises from alcohol in deliquescent crystals, which lose one molecule of water at 100°, presumably changing from the ammonium hydroxide to the cyclic anhydride. It melts at 293° with partial isomerisation to methyldimethylaminoacetate (Willstätter, *l.c.*). It is a very feeble base and neutral to litmus. The *chloride*, $Cl(CH_3)_3N{\cdot}CH_2{\cdot}COOH$, forms leaflets very soluble in water, and peculiar among the chlorides of organic bases in being hardly soluble in alcohol (1 part in 365 c.c. at room temperatures ; separation from choline and other bases). This salt has a strongly acid reaction and has been used as a solid substitute for hydrochloric acid under the name " acidol " in the preparation of tablets, etc. (*cf.* acid pepsin tablets, D.R.P. 172862). When pure it is a convenient standard for alkalimetry. The ***aurichloride***, $C_5H_{11}O_2N{\cdot}HAuCl_4$, the most characteristic derivative, is dimorphous, regular, m.p. 209°, and rhombic, m.p. 248°–250° (Fischer, Ber. 1902, **35**, 1593 ; Willstätter, *ibid.* 2700). The *platinichloride*, $(C_5H_{11}O_2N)_2H_2PtCl_6$, m.p. 242°, crystallises from hot water in anhydrous needles, which in contact with the aqueous mother liquor form four-sided tables with $4H_2O$ (Trier, Z. physiol. Chem. 1913, **85**, 372, who recommends this as a test for betaine). The *picrate*, m.p. 180°, may also be used for the separation from mixtures. A large number of other salts have been described by Stoltzenberg (Z. physiol. Chem. 1914, **92**, 445). Betaine is not a nitrogenous food ; it has no appreciable action on animals, and the part played by it in plant economy is obscure.

Other betaines occurring naturally are : *Stachydrine*,



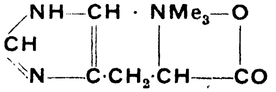
the betaine of α-pyrrolidine carboxylic acid (proline) was discovered in the edible tubers of *Stachys tubifera* (Von Planta, Ber. 1890, **23**, 1699), and occurs in a few other plants. According to Yoshimura and Trier (Z. physiol. Chem. 1912, **77**, 290), the alkaloid chrysanthemine described by Marino-Zuco as occurring in Dalmatian insect powder (*Chrysanthemum cinerariæfolium*) is a mixture of stachydrine and choline. Stachydrine has been obtained synthetically by methylating proline (Engeland, Ber. 1909, **42**, 2962), and from the methyl ester of hygric acid (Trier, Z. physiol. Chem. 1910, **67**, 324).

Betonicine,



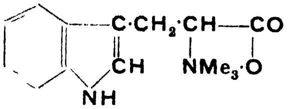
is dextrorotatory oxyproline betaine and *turicine* its stereoisomer. Both occur in *Betonica officinalis* and have been obtained by methylating natural oxyproline (Küng, Z. physiol. Chem. 1913, **85**, 217), and natural 4-hydroxyhygric acid (Goodson and Clewer, Trans. Chem. Soc. 1919, **115**, 923).

Trimethylhistidine,



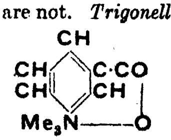
the betaine of histidine, has been obtained from fungi (Kutscher, Zentr. Physiol. 1910, **24**, 775 ; Reuter, Z. physiol. Chem. 1912, **78**, 167), and by the oxidation of *ergothioneine* (Barger and Ewins, Biochem. J. 1913, **7**, 204). The latter base contains an additional sulphur atom in the glyoxaline ring and occurs in ergot (*q.v.*), as well as in mammalian blood corpuscles.

Hypaphorine,



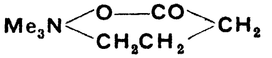
the betaine of tryptophane, occurs in the seeds of *Erythrina Hypaphorus* of Java (Greshoff, Mededeelingen uit's Lands Plantentuin, 1898). For constitution and synthesis, *see* Van Romburgh and Barger, J.C.S. 1911, **99**, 2068.

All the above are derived from α-amino-acids. The next three are not. *Trigonelline*,



the betaine of nicotinic acid, has been found in quite a number of plants, but generally only in very small amount. It probably occurs in many more species. It was discovered in the fenugreek (*Trigonella fœnum græcum*) by Jahns (Ber. 1885, **18**, 2518), who later showed it to be identical with the " methylbetain " of nicotinic acid, already synthesised by Hantzsch (Ber. 1886, **19**, 3140).

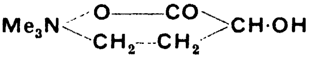
γ-Butyrobetaine,



$$\mathrm{Me_3N}\left\langle\begin{matrix}\mathrm{O{-}{-}CO}\\ \mathrm{CH_2CH_2}\end{matrix}\right\rangle\mathrm{CH_2}$$

was obtained by Takeda (Pflüger's Archiv, 1910, **133**, 365) from dog's urine after phosphorus poisoning (which interferes with the deaminating action of the liver). It is almost certainly identical with one, if not with three, of Brieger's putrefaction bases ("Untersuch. über Ptomaine," i, p. 27, Berlin, 1886), and was first synthesised by Willstätter (Ber. 1902, **35**, 584).

Carnitine, α-hydroxy-γ-butyrobetaine,



$$\mathrm{Me_3N}\left\langle\begin{matrix}\mathrm{O{-}{-}CO}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}\right\rangle\mathrm{CH{\cdot}OH}$$

is a hydroxy derivative of the foregoing, and was isolated from meat extract (yield 1·3%) by Gulewitsch and Krimberg (Z. physiol. Chem. 1905, **45**, 326), and by Kutscher (Z. Unters. Nahr. Genussm. 1905, **10**, 528 ; " novain "). According to the latter, it is identical with a base, $C_7H_{15}O_3N$, isolated from human urine by Dombrowski (Compt. rend. 1902, **135**, 244). Heating with baryta yields trimethylamine and crotonic acid ; phosphorus and hydriodic acid reduce to γ-butyrobetaine. Racemic carnitine was probably synthesised by Fischer and Göddertz (Ber. 1910, **43**, 3272). The small differences from natural carnitine were probably connected with the optical activity of the latter substance.

Myokynine, isolated by Ackermann (Z. Biol. 1912, **59**, 433) from the muscles of horses and dogs, is probably *l*-hexamethyl-ornithine,

$Me_3N(OH){\cdot}[CH_2]_3{\cdot}CH(CO_2H)NMe_3{\cdot}OH$

All the above bases, or at least all the α-betaines, are without marked physiological activity.

For a fuller account of betaines, *see* M. Guggenheim, " Die biogenen Amine," Berlin, 1924. G. B.

BETANIN. The nitrogenous anthocyans isolated as a crystalline hydrochloride from *Beta vulgaris* by Willstätter and Schudel (Schudel Dissertation, 1918, Zürich), who made use of the chloro- and dichloro- picrates. On hydrolysis, betanin yielded the unstable sugar-free pigment *betanidin*, which they were unable to identify satisfactorily. The exact nature of this rare type is now being investigated both analytically and synthetically by Robert Robinson and his collaborators at Oxford. Among the compounds synthesised is *p*-amino-3 : 5 : 7-trihydroxyflavylium chloride, which they are satisfied is not identical with betanidin.

Pigments of the betanin type have been found in the stems of fuchsia and cactus berries and scarlet cactus blooms by Ferdinand Krys (Österr. Chem.-Ztg. 1920, **23**, 55) and in *Bougainvillœa* and *Amaranthus* by Robinson and Robinson (Biochem. J. 1932, **36**, 1649). R. S.-M.

BETEL LEAVES. The dried leaves of a climbing plant in India, Ceylon and Malaya. The volatile oil, 0·2 to 1·0 per cent. of the leaves, contains betel-phenol (chavibetol, an isomeride of eugenol), chavicol, cadinene and sesquiterpenes. Betel has antiseptic carminative and stimulant properties, and is used in India as a masticatory; and by the Malays, who mix the leaves with lime and scrapings of areca nut.

BETEL-NUT *v.* ARECA NUT.

BETITOL, $C_6H_8(OH)_4$, m.p. 224°, and dextrorotatory, is apparently a tetritol (*i.e.* belongs to the cyclitols). It was isolated by V. Lippmann in 1901 from beet molasses. E. F. A.

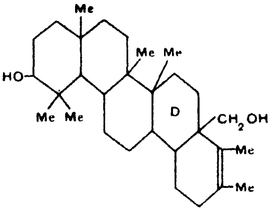
BETOL. Trade name for the β-naphthyl ester of salicylic acid, $C_{10}H_7O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, m.p. 95°. Proposed as an intestinal antiseptic.

BETONICINE *v.* BETAINES.

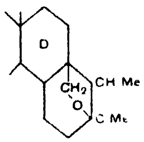
BETORCIN or **β-ORCIN** *v.* BARBATIC ACID.

BETTENDORFF'S TEST *v.* ARSENIC.

BETULIN. This dihydric alcohol (probably I), m.p. 251°, is obtained by solvent extraction of birch bark (Dischendorfer, Ber. 1922, **55**, 3692 ; Vesterberg, Ber. 1923, **56**, 845).



I



II

It is converted into the isomeric allo-*betulin* (II), m.p. 260°–261°, on treatment with formic acid (Ruzicka, Brüngger, and Gustus, Helv. Chim. Acta, 1932, **15**, 634), the constitution of which follows from the observation that whereas betulin is monoethenoid and contains two active hydrogen atoms (Zerewitinoff), *allo*-betulin is saturated and contains but one active hydrogen atom (Ruzicka, Brüngger, Egli, Ehmann, and Goldberg, Helv. Chim. Acta, 1932, **15**, 1496 ; Ruzicka, Hofmann, and Schellenberg, *ibid.* 1936, **19**, 1391; Spring, J.S.C.I. 1936, **55**, 1050). F. S. S.

BETULOL. The sesquiterpene alcohol, *betulol*, $C_{15}H_{24}O$, occurs both in the free state and in combination with acetic acid, in the oil distilled from the leaf buds of *Betula alba*, L. It was first isolated by v. Soden and Elze (Ber. 1905, **38**, 1636) and it has since been investigated by Semmler, Jonas, and Richter (*ibid.* 1918, **51** [B], 417) and by Treibs (*ibid.* 1936, **69** [B], 41). The primary alcohol, b.p. 157°–158°/13 mm., does not appear to be homogeneous, that present in the free state having the constants, d^{20} 0·972, n_D 1·5186, α_D −36°, whilst that isolated after hydrolysis with alkali had d^{20} 0·975, n_D 1·5148, α_D −19·46°. With phosphorus pentachloride betulol yields a *chloride*, $C_{15}H_{23}Cl$, b.p. 160°–170°/11 mm., d^{21} 1·0145, n_D^{21} 1·5208, $[\alpha]_D + 9{\cdot}24°$, which is probably a mixture of a dicyclic and a tricyclic chloride. Oxidation of the alcohol with potassium permanganate results in the formation of a *hydroxy-acid*, $C_{13}H_{20}O_5$, from which by further oxidation with nitric acid a liquid dibasic acid, *betulolic acid*, $C_{10}H_{16}O_4$, and *as*-dimethylsuccinic acid were obtained. Treibs suggests that betulolic acid is a higher homologue of caryophyllenic acid, experimental proof of which has been provided by Ramage and Simonsen (J.C.S. 1937, 74). J. L. S.

BEZETTA. *Tournesol en drapeaux. Schminklappchen. Bezetta rubra et cærulea.* A dye or pigment prepared by dipping linen rags in solution of certain colouring matters. Red bezetta is coloured with cochineal, and is used as a cosmetic (*v.* LITMUS).

BEZOAR. This is the name given to certain concretions found in the stomach or intestines of *Capra aegragus*, a kind of goat; they were formerly prized for their supposed virtue as antidotes to poison.

Oriental bezoars are also found in the gazelle (*Gazella dorcas*) and other ruminants, and form spherical or ovoid masses which range in size from that of a pea to that of a fist; they are destitute of taste and consist sometimes of ellagic and sometimes of -lithofellic acid. Occidental bezoars are found in the lama (*Auchenia glama*) and the vicuna (*A. vicugna*) and consist chiefly of calcium phosphate. German bezoars are obtained from the chamois (*Rupicapra tragus*) and consist chiefly of interlaced vegetable or animal fibres bound together by a leathery coating.

BHANG. The dried leaves of Indian hemp, *Cannabis indica.*

BICUCULLINE *v.* ADLUMINE.

BICUHYBA FAT *v.* MYRISTICA FAT GROUP.

BIEBRICH SCARLET. R. Medicinal. Sudan IV. Scarlet Red. *o*-Toluene-azo-*o*-toluene-azo-*β*-naphthol,

$$C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH,$$

m.p. 184°–185°, first sintering at 175°. Used as an ointment in the treatment of wounds and burns.

BIGNONIA TECOMA.[1] *Tecomin.* The *Bignonia tecoma* is a somewhat common tree in the uplands of Minas, Brazil, which when fully grown is about 30 ft. high and in September is covered with brilliant yellow flowers. The natives mix the sawdust and shavings of this tree with slaked lime, heat the mass with water, and employ the resulting bath to dye cotton cloth. A paste made of the sawdust mixed with lime is also used to stain lighter coloured woods a deep brown. By exhausting the sawdust with boiling 85% alcohol and concentrating the extract, Lee (J.C.S. 1901, 79, 284) isolated the colouring matter *tecomin*, the total amount thus given by the wood being approximately 5%. Tecomin, which has apparently not been submitted to analysis, forms shining chrome-yellow crystals possessing a nacreous lustre, soluble in alkalis with a rose-red coloration.

Nothing is at present known as regards the relationship, if such exists, between tecomin and the colouring matter of chica red or carajura, which originates from the *Bignonia chica.*

A. G. P. and E. J. C.

BIKHACONITINE *v.* ACONITINE AND ACONITE ALKALOIDS.

BILBERRY or WHORTLEBERRY. The fruit of *Vaccinium myrtillus*, one of the moorland shrubs of the *Ericaceæ*. The American variety, known as the blueberry, is described as *V. pennsylvanicum* or *V. vacillans*, probably two sub-species, and is nearly related to the cranberry. The berries are used directly as a fruit, or may be made into wine. The reddish colouring matter which they contain resembles that of the grape in many chemical reactions. For this reason bilberry juice serves to adulterate or add colour to grape wines. Plahl's test (Chem. Zentr. 1908 [i], 1482), a blue coloration produced by heating the extracted pigment with HCl (*cf.* Diemair, *ibid.* 1932, **56**, 247), serves to detect the adulteration. The two pigments may also be distinguished by their absorption spectra. The pigment of the bilberry approximates to the formula $C_{10}H_{12}O_3$, reduces Fehling's solution, and may be oxidised by nitric acid to oxalic and picric acids. Diemair and Lix (Z. Unters. Lebensm. 1933, **66**, 540) record an examination of Plahl's method of detecting the pigment and assume the production from it of phloroglucinol, furfural and protocatechuic acid.

The compositions of the European and American varieties are given as follows :

	European.	American.
Water	76·6–87	83·4
Protein . . .	0·8	0·7
Free acid . . .	1·1–1·7	—
Sugar	3·8–6·8	—
Pentosans, etc. .	0·6–1·4	-
N-free ext. . .	—	13·5
Fibre	3·7–12·0	3·2
Ash	0·3–1·0	0·4

The sugar, according to Windisch (Z. Nähr. Genussm. 1908, **8**, 347), consists almost entirely of invert sugar, sucrose representing 3–5% of the total. The ripening of Alsatian berries is marked by a considerable increase in reducing sugars but only a small change in sucrose (Ann. Falsif. 1934, **26**, 12).

The composition of bilberry juice is shown by analyses of Windisch and of Feder to fall within the following limits : solids 7·0–11·4, protein 0·09–0·3, acids 0·9–1·2, invert sugar 3·9–8·8, sucrose 0·0–0·26, ash 0·2–0·3%.

The acids appearing in the fruit are given by Kaiser (Suddeut. Apoth.-Ztg. 1925, **65**, 48) as, citric 72·4, malic 18·7, succinic 4·87, lactic 0·81, oxalic 0·16, and quinic (?) 2·68%. [Other published analyses include Kunz and Adam (Z. Unters. Nähr. Genussm. 1906, **12**, 670); Behre, Grosse, and Schmidt (Chem. Zentr. 1909 [i], 456); Muttelet (Ann. Falsif. 1924, **17**, 454); Nelson (J. Amer. Chem. Soc. 1927, **49**, 1300).

---

[1] According to Holmes the name *Bignonia tecoma* does not appear in the Kew Index, but only *Bignonia tecomoides*, which is, however, a shrubby species.

Fatty matter obtained from bilberries includes a wax, m.p. 71°, and (from the seed) a drying oil, *d* 0·9331, *n* 1·478, Reichert-Meissl val. 0·66, Polenske val. 0·30, acid val. 3·82, hexabromides of linoleic and linolenic acids 28·5%.

According to Kulish the ash analysis is: K_2O 32·9, MgO 5·9, CaO 8·7, P_2O_5 12·8%.

A. G. Po.

BILE. Bile is the secretion of the liver which is poured into the duodenum, the first part of the small intestine. It can be collected in animals by means of a biliary fistula ; the same operation has occasionally been performed in human beings. After death the gall bladder yields a good supply of bile, which is more concentrated than that obtained from a fistula. The amount of bile secreted is differently estimated by different observers, in man it probably varies from 500 to 1,000 c.c. per diem.

Its constituents are the bile salts proper (sodium glycocholate and taurocholate), the bile pigments (bilirubin and biliverdin), a mucinoid substance, small quantities of fats, soap, cholesterol, lecithin, urea, and mineral salts, of which sodium chloride and the phosphates of calcium and iron are the most important.

Bile is a yellowish, reddish-brown, or green fluid, according to the relative preponderance of its two chief pigments. It has a musk-like odour, a bitter-sweet taste, and is alkaline to litmus. The specific gravity of human bile is 1·026 to 1·032 from the gall bladder, and about 1·011 when derived from a fistula. The greater concentration of gall-bladder bile is partly explained by the addition to it from the wall of that cavity of the mucinoid material it secretes. The following table will, however, show that the low percentage of solids in fistula bile is due mainly to paucity of bile salts. This is accounted for in the way first suggested by Schiff—that there is normally a bile circulation going on in the body, a large quantity of the bile salts that pass into the intestine being first split up, then re-absorbed and again synthesised and secreted. This would obviously be impossible in cases where all the bile is discharged to the exterior through a fistula. The following is the table in question, the results being the mean of several analyses of human bile :

Constituents	Fistula bile. %	Gall-bladder bile. %
Bile salts	0·42	9·14
Cholesterol, lecithin, fat	0·07	1·18
Mucinoid material . .	0·17	2·98
Pigment	0·07	
Ash	0·66	0·78
Total solids . . .	1·39	14·08
Water (by difference) .	98·61	85·92

For methods of analysing human bile, *see* v. Czyhlarz, Fuchs, and v. Fürth (Biochem. Z. 1913, **49**, 120 ; Analyst. 1913, 208). Hoppe-Seyler/Thierfelder, " Physiologisch und Pathologisch Chemische Analyse," Springer, Berlin, 1924 ; Peters and van Slyke, " Quantitative Clinical Chemistry," Baillière, Tindall and Cox, London, 1931.

THE BILE SALTS.—The sodium salts of glycocholic and taurocholic acids are those most frequently found. The former is more abundant in the bile of man and herbivora, the latter in carnivora. *Glycocholic* acid, $C_{26}H_{43}NO_6$ (sodium salt, $C_{26}H_{42}NaNO_6$), is by the action of dilute alkalis and acids, and also in the intestine, hydrolysed and split into glycine (amino-acetic acid), and cholic acid,

$$C_{26}H_{43}NO_6+H_2O=C_2H_5NO_2+C_{24}H_{40}O_5$$

Taurocholic acid, $C_{26}H_{45}NO_7S$ (sodium salt, $C_{26}H_{44}NaNO_7S$), similarly splits into taurine (amino-ethyl sulphonic acid) and cholic acid,

$$C_{26}H_{45}NO_7S+H_2O$$
$$=C_2H_4{\cdot}NH_2{\cdot}HSO_3+C_{24}H_{40}O_5$$

These substances usually are detected by Pettenkofer's reaction ; small quantities of cane sugar and sulphuric acid added to the bile produce a brilliant purple colour. This is due to the interaction of furfuraldehyde (produced from the sugar and sulphuric acid) and cholic acid.

Throughout the animal kingdom considerable variations are found in the bile salts. Thus in many fishes potassium instead of sodium salts are present. There are also variations in the bile acids themselves, as is shown in the following table :

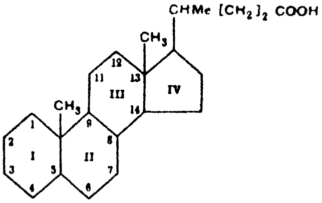
THE BILE ACIDS.

Name.	Formula.	Sources.	Structure.
Cholic acid	$C_{24}H_{40}O_5$	Man, ox, goat, sheep, antelope.	3 : 7 : 12-Trihydroxy-cholanic acid
β-Phocæcholic acid	$C_{24}H_{40}O_5$	Walrus, seal	
Deoxycholic acid	$C_{24}H_{40}O_4$	Man, ox, goat, sheep, antelope, deer	3 : 12 - Dihydroxy-cholanic acid
Chenodeoxycholic acid	$C_{24}H_{40}O_4$	Man, ox, goose, hen	3 : 7 - Dihydroxy-cholanic acid
Hyodeoxycholic acid	$C_{24}H_{40}O_4$	Pig	3 : 6 - Dihydroxy-cholanic acid
Lithocholic acid	$C_{24}H_{40}O_3$	Man, ox	

THE BILE ACIDS.—The bile acids have furnished in recent years a field of great interest in constitutional chemistry. Close structural similarities have been demonstrated between these acids and the various sterols of plant and animal origin. Numerous bile acids occur in bile derived from different animal sources, as is indicated in the above table of representative acids.

Among others which have been characterised but await detailed investigation are *α-phocæcholic acid* from the walrus, *ursocholic acid* from the polar bear, *fellic acid* from man, and a *tetrahydroxycholanic acid*.

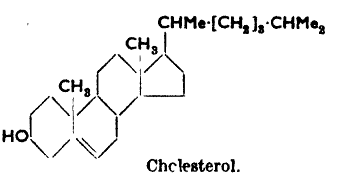
The names of Mauthner, Windaus, Wieland, Borsche and Diels are especially associated with the earlier structural investigations of the bile acids. The later work of Rosenheim and King and of Wieland and his collaborators and the suggestions based thereon have led to the elucidation of the basic structure of the bile acids as a phenanthrene nucleus associated with a fourth five-membered ring to which is attached the side chain, as follows:



THE BILE PIGMENTS, *q.v.*

BILE MUCIN.—The viscous material in the bile of some animals (*e.g.* man) is true mucin; in other (*e.g.* the ox) it is a nucleoprotein.

CHOLESTEROL.—Of the other constituents of the bile cholesterol is the most interesting; although normally present in traces only, it may occur in excess and form the concretions known as gallstones, which are usually more or less tinged with bile pigment. It is a monoatomic unsaturated alcohol, with the empirical formula $C_{27}H_{45}{\cdot}OH$. Its structure has been elucidated as a cognate problem in the investigations already referred to in this article which have been carried out on bile acids, sterols and other members of the cholane series.



Cholesterol.

Its formula, shown above, illustrates the close structural relationship between the bile acids and cholesterol.

THE PHYSIOLOGICAL USES OF BILE.—Bile is doubtless to some extent an excretion. Some state that it has a slight lipolytic action; and in some animals it certainly has a feeble diastatic power. Its main action, however, is to assist pancreatic digestion; this it does, not only because its alkalinity is useful in helping to neutralise the acid mixture which leaves the stomach (chyme), but it also aids the action of the enzymes of pancreatic juice. This is true for the proteolytic enzyme (trypsin), and the amylolytic enzyme (amylopsin), but is especially so in the case of pancreatic lipase.

In virtue of the properties which the bile salts possess of lowering surface tension, the products of fat-cleavage pass more rapidly through membranes moistened with bile than through these which are not. There is a good deal of evidence that the same holds *in vivo*, and thus the presence of bile aids the absorption of fats by the mucous membrane which lines the intestinal wall. Bile also is a solvent of fatty acids. J. Mellanby (J. Physiol. 1927 *et seq.*) has accumulated much interesting information which suggests that, in the presence of bile, unhydrolysed fats and unsaponifiable lipoids may be adsorbed from the intestine in a particulate condition.

When the bile meets the chyme, the turbidity of the latter is increased owing to the precipitation of unpeptonised protein. This action of the bile salts is probably useful, as it converts the chyme into a more viscid mass and somewhat hinders its progress along the first part of the intestine, so allowing digestion and adsorption to occur there.

Bile is said to be a natural antiseptic, but it is very doubtful if it is really efficient in reducing the putrefactive processes in the bowel. The bile salts are *in vitro* very feeble germicides, and the bile itself is readily putrescible; any power it may have in lessening putrescence in the intestine is due chiefly to the fact that by increasing adsorption it lessens the amount of putrescible material in the intestinal tract. It is stated also that bile increases the peristaltic action of the large intestine.

INDUSTRIAL AND COMMERCIAL USES OF BILE.—Apart from a somewhat limited use as a therapeutic agent, bile has but little commercial importance. It is, however, employed for cleansing woollen goods, and, as housekeepers know, is specially useful in cleaning carpets. This is probably connected with its power of lowering surface tension. Bile is also used by artists to ensure the uniform spreading of water colours on paper. J. P.

BILE PIGMENTS.—Bile pigments are excreted normally by the liver into the bile, the latter being formed by the liver and poured into the duodenum. The bile owes its yellowish, reddish-brown or green colour to the biliary pigments, the colour being determined by the relative quantities of the two chief pigments—*bilirubin* and its oxidised form, *biliverdin*. Rich (Physiol. Rev. 1925, **5**, 182) sums up present information on the question of the formation of bile pigment in the following statement: "Hæmoglobin may be regarded as a source of bile pigment and we have no proof that there are other sources. There is no proof that the epithelial liver cells can form bile pigments under any circumstances; on the other hand, it is certain that the pigment can be formed outside of, and independently of, the activity of the liver cells. There is evidence that cells of the reticulo-endothelial type can form bile pigment, but this evidence is not yet complete enough to be regarded as proof. There is no evidence whatever that any other type of cell can form the pigment, nor is there any proof that the pigment can be formed extracellularly by enzyme action."

The chief evidence for the statement that bile pigments are formed from hæmoglobin *in vivo* may be summarised as follows:

(1) Intravascular hæmolysis of red blood cells produced by the injection of hæmolytic agents causes appearance of bilirubin in the urine.

(2) Injection of hæmoglobin into an animal with a biliary fistula leads to excretion of bile pigments by the liver.

(3) Excessive quantities of hæmoglobin, formed in tissues under pathological conditions, are accompanied by increased appearance of bile pigments.

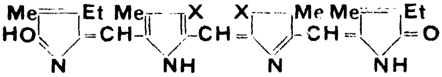
It is, however, possible that bile pigments may also owe their origin to breakdown of cytochrome or to degradation of chlorophyll ingested in vegetable matter.

Bilirubin, $C_{33}H_{36}O_6N_4$, is best obtained from ox gallstones. It differs from hæmin by having in its molecule one carbon atom less, two oxygen atoms more, and no iron. It is characterised by colour reactions, *e.g.* Gmelin's, in which nitric acid containing nitrite is added to a solution of the pigment in chloroform. The solution passes through the colour changes green, blue, violet, red and yellow. Bilirubin has no characteristic absorption spectrum ; hence the ring system of the porphyrin group is probably absent.

On oxidation with chromic acid bilirubin gives hæmatic acid, and on reduction with HI cryptopyrrole and cryptopyrrolecarboxylic acid are yielded. Gentle reduction yields *mesobilirubin*, $C_{33}H_{40}O_6N_4$, which on further reduction gives *mesobilirubinogen* (*urobilinogen*). The latter substance is found in normal bile and urine and in considerable quantities in certain pathological urines. Under the action of air and light urobilinogen is transformed into a yellow pigment *urobilin*. This pigment is probably identical with the stercobilin found in fæces. It is possible that urobilin is not a simple substance but a mixture of pigments formed from the precursor chromogen. Urobilinogen may be detected by an intense colour reaction with Ehrlich's *p*-dimethylaminobenzaldehyde reagent.

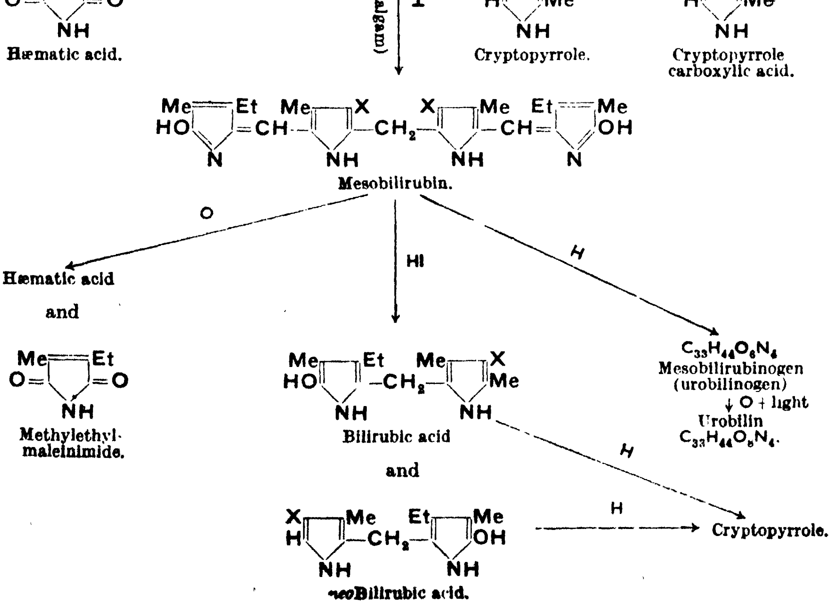
A summary of the reactions undergone by bilirubin and its derivatives is shown below. Our knowledge of this subject is derived chiefly from the work of H. Fischer and his colleagues (*e.g.* Siedel and Fischer, Z. physiol. Chem. 1933, **214**, 145).

It is clear from the formula given for bilirubin that the latter represents a biological oxidation product of hæmin, which undergoes breakdown by fission of an α-methine bridge, two α-hydroxyl groups being introduced. The blue phase, which is a characteristic part of Gmelin's reaction for bilirubin and mesobilirubin, is ascribed to the substance " glaucobilin," which is probably



Glaucobilin. (X = $-CH_2{\cdot}CH_2{\cdot}COOH$.)

(Fischer *et al.*, Z. physiol. Chem. 1932, **206**, 201).



Lemberg isolated *uteroverdin* from dog placenta and assigned to it the constitution of a dehydrobilirubin. The pigment of seagull's eggs has been identified with uteroverdin by Lemberg. The latter's observations (Lemberg, Annalen, 1933, **505**, 160) on chromoproteins of red algæ or seaweeds are of interest in that they show that such substances (*e.g.* phycocyan and phycoerythrin) yield on boiling with 10% methyl alcoholic potash, glaucobilin.

Watson (Z. physiol. Chem. 1932, **204**, 57; **206**, 101) first succeeded in isolating stercobilin as well as *copromesobiliviolin* and *copronigrin* from human excrement. Recently it has become possible to obtain crystalline urobilin from urine, and there are clear indications that urobilin and stercobilin are identical (Watson, Z. physiol. Chem. 1933, **221**, 145). The reader is referred to recent work by Lemberg (Biochem. J. 1935, **29**, 1322) on the origin of bile pigments from haemins. J. H. Q.

BILIPOSOL. A basic α-carbethoxy-β-methylnonoate of bismuth. A lipo-soluble bismuth compound yielding a clear, homogeneous oily solution. Antiluetic.

BILIRUBIN *v.* BILE PIGMENTS.

BILIVAL. Sodium lecithino-cholicum. A chemical combination of lecithin and sodium cholate. Cholagogue.

BILIVERDIN *v.* BILE PIGMENTS.

BI-NA-GLUCONATE. Bismuth sodium gluconate, colloidal. A soluble bismuth salt in colloidal solution. Antiluetic.

BIOS, the name given by Wildiers and his colleagues (1901) to a substance or group of substances stimulating the growth of yeast and held by later workers to be analogous to the vitamins which are needed by higher organisms. It is now known that, just as the vitamin needs of animals are complex, so the growth stimulants for yeast are also of a diverse character, and, indeed, may vary greatly according to the type of yeast used. (For further details, *see* "Annual Review of Biochemistry," vol. I, 1932, and subsequent issues.) L. J. H.

BIOTITE *v.* MICA.

BIRCH-BARK OIL. This is the oil of wintergreen of commerce, and consists almost entirely of methyl salicylate. It is obtained by distillation from the bark of the sweet birch, *Betula lenta* (Linn.), N.O. Betulaceæ. The bark is first macerated in water for 12 hours, when the glucoside *gaultherin* is decomposed by the ferment betulase which is present in the bark, with the formation of methyl salicylate. The yield of oil is 0·4 to 0·6%.

Characteristics.—Sp.gr. 1·182–1·192, optically inactive, n_D^{20} 1·534–1·538. Ester content not less than 98%. It gives a deep blood-red colour with the following test: to 0·5 c.c. of the oil add 0·5 c.c. of a 5% solution of vanillin in alcohol, shake well, add 2 c.c. strong sulphuric acid and again shake. This reaction distinguishes the natural oil from artificial methyl salicylate.

Birch-bark oil is used medicinally for the treatment of acute rheumatism and sciatica, both internally (in doses of 5 to 15 minims), and externally as a linament. C. T. B.

BIRCH TAR OIL. *Oleum rusci*, *Oleum betulæ albæ*. Oil of White Birch. The tar obtained by the destructive distillation of the wood and bark of *Betula alba* is allowed to stand when the oil separates. It is a dark, thick liquid with an odour of "Russian leather," for the preparation of which it is used. Sp.gr. 0·920 to 0·955; ester content not less than 70%. Its solution (1 in 20) in light petroleum should not give a greenish colour on shaking with 0·1% solution of cupric acetate (absence of fir tar). Used in ointments for eczema and other skin diseases.

BIRD LIME (*Glu*, Fr.; *Vogelleim*, Ger.) is a green or grey tough adhesive mass, which pulls into threads, and is largely soluble in ether, benzene, and carbon bisulphide. According to Theophrastus, the elder Pliny (A.D. 23–79), the herbals of the Middle Ages, and much scientific and popular literature, bird lime is made from mistletoe berries; a source which seems the more probable on account of the derivation of the words "viscous," "viscosity," from *Viscum album*, the mistletoe. Tubeuf ("Monographie der Mistel," R. Oldenburg, Munich and Berlin, 1923, p. 49), after exhaustive inquiries among foresters, could obtain no evidence of this preparation. F. Schiller (Sitzungsber. Akad. Wiss. Wien, Math. Naturw. Kl. Abt. 1, 1928, **137**, 243) confirmed the experimental results of Lenz (Botanik der alten Griechen und Römer, Gotha, 1859, 599) and failed to prepare an adhesive from mistletoe berries or bark. The berries yielded a cellulose slime which dried to a brittle mass. Tubeuf and Schiller consider that the bird-lime of the early authorities was made from the berries of *Locanthus europæus*, a parasitic plant of the mistletoe family. From these berries, which contain when dried 36% caoutchouc, Schiller prepared a strongly adhesive substance. This plant, however, is found only in southern and south-eastern Europe and the bird lime of northern European countries is made from the inner bark of the common holly, *Ilex aquifolium*, by macerating it with water and allowing the mixture to stand for some days, or by burying the bark in the earth and subsequently scraping off the adhesive from the inner surface. According to Divers and Kawakita (J.C.S. 1888, **53**, 268) white Japanese bird lime from the holly species *Ilex integra* contains the palmitic esters of two alcohols, *mochyl alcohol*, $C_{26}H_{46}O$, m.p. 234°, and *ilicyl alcohol*, $C_{22}H_{38}O$, m.p. 172°, as well as a small quantity of caoutchouc (*cf.* Yanagisawa and Takashima, Chem. Zentr. 1922 iii, 166). Macaire (J. de Pharmacie, 1834, **20**, 20) and also Reinsch (Chem. Zentr. 1861, 145) prepared a viscous substance "viscin" by macerating with water the bark of either holly or mistletoe. Their analyses do not agree, but the name appears in the later literature (*cf.* Einleger Fischer, and Zellner, Sitzungsber. Akad. Wiss. Wien, 1923, Abt. ii, b, **132**, 263).

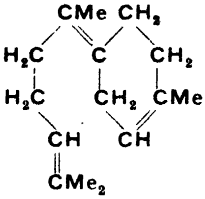
Adhesive preparations termed bird lime have been made by boiling linseed oil, and also from glue and zinc chloride solution. The use of bird lime or similar adhesive for snaring birds is illegal in England (Protection of Birds Act, 1925). J. N. G.

BIRMABRIGHT *v.* Alloys, Light.

BIRMASIL *v.* Alloys, Light.

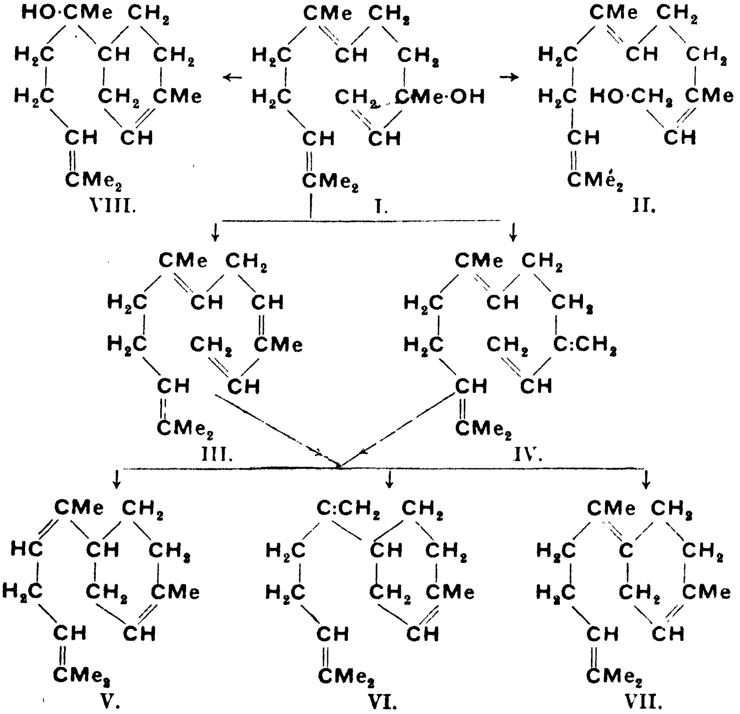
BISABOL *v.* Bisabolene and Gum Resins.

BISABOLENE,



The sesquiterpene hydrocarbon *bisabolene*, $C_{15}H_{24}$, is, with the exception of cadinene, probably the most commonly occurring sesquiterpene constituent of essential oils. It was first separated by Tucholka (Arch. Pharm. 1897, **235**, 289) from Bisabol myrrh, and later by Burgess and Page (J.C.S. 1904, **85**, 414) from bergamot oil. Its presence has also been reported (*inter alia*) in camphor oil, citronella oil, Siberian pine needle oil and opoponax oil. It is a colourless, somewhat viscid oil, b.p. 133°–134°/12 mm., $d_{4°}^{21°}$ 0·8717, $n_D^{21°}$ 1·4923, and it is readily characterised by the preparation of its *trihydrochloride*, m.p. 79°–80°. It can be regenerated from this derivative by warming with sodium acetate in acetic acid.

The constitution of bisabolene has been proved by the investigations of Ruzicka and Capato (Helv. Chim. Acta, 1925, **8**, 263) and of Ruzicka and van Veen (Annalen, 1929, **468**, 133, 143). When *dl*-nerolidol (I) is digested with acetic acid it gives in addition to the primary alcohol, farnesol (II), a mixture of two acyclic hydrocarbons, α- and β-farnesenes (III and IV), from which, by further treatment with formic acid, a monocyclic hydrocarbon, or mixture of hydrocarbons, is obtained which gives with hydrogen chloride *bisabolene trihydrochloride*. From its method of preparation this hydrocarbon must be represented by one of the structures V, VI, or VII. Since on oxidation the natural hydrocarbon, and also that regenerated from the trihydrochloride, yields acetone and levulinic acid, it follows that it must consist essentially of γ-bisabolene (VII). β-Bisabolene (VI) does not appear to be formed, but evidence was obtained of the presence of α-bisabolene (V).



Confirmation of the structure assigned to bisabolene has been obtained by a direct synthesis from α-terpineol (Ruzicka and Liguori, Helv. Chim. Acta, 1932, **15**, 3).

Bisabolol is the name given to a tertiary alcohol, b.p. 154°–156°/12 mm., $d_{4°}^{18°}$ 0·9216, $n_D^{17°}$ 1·4939, formed as a by-product in the conversion of nerolidol to farnesene. It has most probably the structure (VIII). J. L. S.

BISCINIOD. Insoluble powder prepared by mixing a solution of a cinchonidine salt with bismuth and potassium iodide solutions.

BISMAL. Bismuth methylene digallate (*v.* Bismuth).

BISMARCK BROWN *v.* DYESTUFFS, Azo.

BISMARSEN. Sulpharsphenamine bismuth; bismuth arsphenamine sulphonate. The sodium salt of the bismuth derivative of arsphenamine methylene sulphonic acid,

$$C_{21}H_{21}O_{12}As_3Na_3S_3N_3Bi_2$$

Antisyphilitic.

BISMITE or BISMUTH-OCHRE. Native bismuth oxide, Bi_2O_3, occurring as a yellow earthy powder, or as minute rhombohedral scales. Analyses of various bismuth-ochres from the tourmaline mines of San Diego Co., California, show these to be either bismuth hydroxide, $Bi(OH)_3$, or pucherite, $BiVO_4$, or mixtures of these; and doubt has been expressed as to the occurrence of the pure oxide, Bi_2O_3, in nature (W. T. Schaller, 1911).
L. J. S.

BISMOCLITE. Bismuth oxychloride, $BiOCl$, found as grey nodules with bismuth ores in pegmatite near Jackals Water, Steinkopf, Namaqualand, South Africa. X-ray examination shows the mineral to be tetragonal (E. D. Mountain, Min. Mag. 1935, 24, 59). L. J. S.

BISMO-CYMOL. Basic bismuth camphorcarboxylate. A solution in olive oil of a basic bismuth derivative of campho-carboxylic acid, $(C_{10}H_{15}O{\cdot}CO_2)_3Bi_2O(OH)$. Antiluetic.

BISMOGENOL. Basic bismuth salicylate, $C_6H_4(OH)COO{\cdot}BiO$, in oily suspension. Antisyphilitic.

BISMOID. A stabilised suspension of finely divided bismuth metal in sterile aqueous medium. Antiluetic.

BISMUTH. (*Etain de glace*, Fr.; *Wismuth*, Ger.) Symbol Bi. At. wt. 209·0; at. no. 83.

Occurrence.—Bismuth occurs in small quantities in widely distributed localities, usually with other ores, such as those of tin, copper, cobalt, gold, silver, lead, and frequently with tungsten, molybdenum, and uranium (*v.* BISMITE, BISMUTITE, BISMUTOTANTALITE).

Bismuth occurs in the native state and this with the sulphide, bismuth glance or *bismuthinite*, Bi_2S_3, constitute its chief sources of supply, and are obtained principally from Bolivia, where native metal, the sulphide and their oxidation products are found, always associated with tin ores. A single mine in Bolivia could readily flood the world's markets, as the normal demand varies from 300 to 500 tons per annum only.

From Peru bismuth is exported in the form of concentrates containing about 20% bismuth and also as a lead-bismuth alloy. The Cerro de Pasco Copper Co. is a large potential producer of the metal. Some 20,000 tons of fume containing 2% bismuth and 40% lead are said to have been accumulated there.

In Canada bismuth is found as a minor constituent of several ores and small quantities have been recovered in the treatment of the silver-cobalt-nickel ores of Ontario.

In New South Wales bismuth ores are found in quartz pipes developed in siliceous granites near the contact with basic igneous or sedimentary rocks; they are usually associated with molybdenite and less commonly with tin or tungsten minerals. In Queensland the occurrences seem to be somewhat similar, but the bismuth typically accompanies wolframite. Native bismuth also occurs in the Owen goldfield, New Zealand.

Deposits of bismutite and bismuth ochre are being worked on an increasing scale in China, and in Japan there are scattered occurrences of bismuth ore which may be associated with ores of tungsten and molybdenum and also with gold, silver, and copper.

Bismuth is widely distributed in Northern Rhodesia; many of the gold ores contain the metal, which is not recovered. Bismuth is also associated with the copper in the large copper deposits.

Spain is probably the leading European source of bismuth ore, where it is found associated with cobalt, nickel, lead, copper and silver.

Practically all the bismuth produced in the United States of America is obtained from the treatment of slimes resulting from the refining of lead bullion by the Betts' electrolytic process. Flue dust at many plants also constitutes a potential source of supply and there has been a tendency for the supply to exceed the demand (U.S. Bureau of Mines, Information Circular 6466, 1931).

Extraction.—Bismuth ores, after a preliminary concentration by hand-sorting or gravity methods, are further treated by dry or by wet methods. Liquation processes were formerly used in Saxony, but proved to be wasteful and have been superseded by smelting methods; owing to the easy volatility of the metal and its oxide smelting has to be carried out at the lowest possible temperature. Wet processes are usually based on the fact that bismuth oxychloride is readily precipitated by hydrolysis of chloride solutions.

Liquation.—In this process formerly used the native metal was separated as far as possible from the gangue by melting at a low temperature. The picked ore was broken into pieces as large as hazel nuts, and placed in inclined iron tubes in charges of about 12 cwt., sufficient space being left in the tube for stirring the ore from the upper end. The tubes were closed at the upper ends by plates of iron, and at the lower ends by similar plates containing circular apertures through which the molten metal ran. The ends of the tubes projected slightly beyond the walls of the furnace, the upper over a tank and the lower ends over iron crucibles which contained powdered charcoal, and which were gently heated from below by a small charcoal furnace. The tubes were heated so as to cause the metal to flow easily, and in about 10 minutes the bismuth began to pass out into the crucibles, being there covered by the charcoal and thus protected from oxidation. The ore was occasionally stirred with an iron rod from the upper end, and in from 30 to 60 minutes the operation was completed. The residues, *graupen* or *bismuth barley*, were raked from the upper end into the tank, and at once replaced by fresh ore. In this manner only about two-thirds of the bismuth was extracted, the compounds being unreduced. The contents of the pots were removed by ladles to moulds and cast into ingots of 25 to 50 lb. weight.

Smelting.—In the smelting of bismuth ores and residues reverberatory furnaces, shaft furnaces or crucibles are used according to the nature and quantities of materials to be treated.

In reverberatory furnace smelting, the concentrates from Bolivia, Australia, etc., which contain native bismuth and also the sulphide are submitted to an oxidising roast for the removal of the sulphur and the oxide is subsequently reduced by the addition of carbon. Iron also is generally added to the charge for the reduction of any remaining sulphide. Only small furnaces are used and the temperature is kept fairly low, as otherwise volatilisation losses may become serious. Extraneous matters are removed in the form of a slag which must necessarily have a low melting point, and for this purpose sodium carbonate, lime, oxide of iron and fluospar are added as fluxes. The metallic bismuth obtained is sometimes partially refined by fusing on an inclined iron plate, allowing the metal to run down, leaving behind a dross containing most of the impurities.

Shaft furnaces are used in Bolivia for the smelting of bismuthinite ores which are rich enough for this treatment. The cylindrical furnaces used have a smelting column of 15 ft. from the tuyeres to the top and a hearth area of 12½ sq. ft. The charge consisting of ore, fuel, iron and fluxes is run down, and crude metallic bismuth, slag and flue dust containing a considerable amount of bismuth are obtained. This flue dust is collected and exported for recovery of its bismuth contents (T. L. Johnston, Metal Ind. 1933, **43**, 174).

Crucibles are also largely used for the smelting of rich ores, concentrates and by-products containing bismuth. Clay crucibles capable of treating 1 cwt. or more are used, and these may be heated in coke or gas-fired furnaces. The charges used differ widely according to the nature of the material under treatment, carbon being added for the reduction of oxide, iron turnings for reduction of sulphide, sodium carbonate, lime and fluorspar as fluxes. The heating is continued until tranquil fusion is obtained and the whole is then poured into conical moulds. The liquid separates into three layers, the upper consisting of slag which contains little or no bismuth, the middle of a speiss containing arsenic, sulphur, nickel, iron, etc., with about 2% of bismuth, and the lower consisting of bismuth metal which is further refined according to the uses to which it is to be put.

Rich ores of bismuth containing up to 60% of bismuth are imported into England for treatment and are usually fused down in plumbago crucibles with borax and sodium carbonate as fluxes and crude tartar as reducing agent.

The bismuth present in small quantities in lead, copper and tin ores frequently becomes concentrated in the secondary products of the metallurgical processes and may then be profitably extracted. The products of ordinary smelting operations that contain bismuth are the flue dust and condensed fume from the smelting furnaces, especially when steps are taken to make this condensation of fume efficient, as by filtering or electrical precipitation processes used, for example, during the smelting of lead and copper ores.

Other classes of important by-products from metallurgical operations which are possible sources of bismuth are the anode slimes from the electrolytic refining of metals such as lead and copper.

There are also secondary products obtained during the treatment, other than electrolytic, of certain metals, from which bismuth may be obtained profitably, and these include lead, silver and especially argentiferous lead.

The treatment of flue dusts and condensed fume may be carried out by dry or by wet processes and the exact method will depend on their composition. For the dry way they are compressed into briquettes with suitable additions and returned to the main smelting operation, whereby the chief metallic contents are recovered and bismuth further concentrated in the fume, which is treated for bismuth when it contains sufficient of this metal.

For the treatment of anode slimes from the electrolytic refining of lead which contain bismuth, antimony, arsenic, silver, gold together with résidual lead, the first step is the removal of the more oxidisable constituents. This may be effected by a fusion, using sodium carbonate and sodium hydroxide as fluxes ; this fusion removes arsenic and lead and if copper is present sodium sulphide is also added to the charge to convert the copper into sulphide which is then carried into the slag. The metal thus obtained contains the bismuth, silver and gold, together with any antimony that may have been present, and is cast into slabs which are made the anodes for a second electrolytic refining process which is carried out in porcelain tanks. The electrolyte used consists of bismuth chloride solution containing excess of hydrochloric acid, and the cathodes may be of pure bismuth obtained from a previous run or of graphite.

Bismuth is dissolved at the anode and deposited at the cathode as pure metal, while the gold, silver and antimony present are left as anode slimes which are collected, treated with hydrochloric acid for the removal of antimony and any remaining bismuth and then washed, dried and melted down to crude bullion.

The anode slimes recovered from electrolytic copper refining are much less important as a source of bismuth but in some cases contain sufficient for it to be recovered profitably.

Argentiferous lead obtained by ordinary smelting processes is a source of bismuth, and when the Pattinson process is used for the concentration of the silver the bismuth is, at the same time, concentrated with the silver in the remaining molten lead.

The further treatment of this concentrated argentiferous lead is a cupellation process in which the lead is preferentially oxidised and removed, silver remaining. During this process the lead oxidises much more rapidly than bismuth and towards the end of the process, a blackish litharge rich in bismuth is formed which may contain up to 25% bismuth oxide and is treated for the recovery of the metal. This litharge, together with the bottom portions of the cupel rich in bismuth, is treated with hydrochloric acid, bismuth chloride being formed. The solution is filtered and excess of water is added to precipitate the metal as bismuth oxychloride; the precipitate is collected, washed, dried and reduced to metal by fusion with charcoal, sodium carbonate, powdered glass, etc., being added as fluxes.

The removal of bismuth from lead may be carried out by a process similar in principle to the Parkes' process for the desilverisation of lead, in which the lead is raised in temperature to the melting-point of zinc, and zinc added and stirred well into the lead. On allowing to stand, the zinc rises to the surface as a dross and carries the silver with it. In the case of bismuthiferous lead, calcium or a calcium alloy is used instead of zinc, and the dross formed is found to carry the bismuth to the surface. The process was invented by G. J. Kroll of Luxemburg, who obtained a patent in 1922, and since then it has been developed in America (Chem. Age, 1932, **26**, Feb., Met. Sec., p. 7).

By the treatment of lead containing 0·2% bismuth a purified lead is obtained containing less than 0·05% bismuth, and a dross containing 5% of the metal together with certain other impurities originally present in the lead. The dross is melted down under reducing conditions and the metal obtained is treated by the Betts' electrolytic process and the bismuth recovered.

In a series of eight Betterton patents, calcium, barium and zinc are employed to debismuthise lead bullion (U.S.P. 1853534–41, Ap. 12, 1932).

Wet methods of extracting bismuth from minerals, waste products of smelting operations, residues from the refining of other metals, etc., are largely used.

In the case of minerals containing sulphides, these are given a preliminary roast to convert the bismuth to oxide. Carbonate of bismuth, oxides, and the various residues containing oxides are treated with hydrochloric acid for the solution of the bismuth which is afterwards recovered by means of metallic iron which replaces it from solution, or by dilution with water which causes the precipitation of oxychloride as described above.

Other methods which have been used for the solution of bismuth from sulphide ores include treatment with a solution of an alkali or alkaline earth hyposulphite. The solution thus obtained is treated with alkali sulphides and the resulting precipitate of bismuth sulphide is dried and smelted or otherwise treated.

Ferric chloride solution has been used as a solvent for bismuth sulphide, the resultant solution being treated for the precipitation of the bismuth by iron or zinc or by electrolysis.

A mixture of sulphuric acid, water, common salt and potassium nitrate has also been used as the extracting liquor, the bismuth being finally obtained as the oxychloride, which may be sold as such or reduced to the metallic state.

Since the principal use of bismuth is in medicinal or pharmaceutical preparations, it is necessary that the metal should be of a high degree of purity and especially free from lead and arsenic.

One method which has been largely used, and is still used to a considerable extent, consists of the repeated precipitation and solution of the oxychloride, particular care being taken for the elimination of lead and arsenic. Metallic bismuth refined entirely by electrolytic or dry processes is now on the market, however, and this is the best material with which to begin the preparation of medicinal compounds.

Precipitated bismuth for pharmaceutical purposes may be obtained by the reduction of a solution of bismuth trichloride in hydrochloric acid by means of hypophosphorous acid. It contains not less than 98·5% metallic bismuth and consists of a dull grey powder easily diffusible in water. When mixed with water and examined microscopically no particles with a diameter greater than 15 microns are seen to be present (Brit. Pharm. 1932, p. 91).

Purification.—Much attention has been and is now being given to the purification of metallic bismuth obtained by the various methods already described; the method of purification to be used will depend on the source of the metal and the method by which it has been extracted; for example, the metal obtained by smelting methods from ores and other products will contain larger quantities of impurities than the metal obtained by electrolytic processes. The method of purification to be used may also vary according to the uses to which it is to be put, although for general market purposes a high degree of purity is usual.

There are no standard specifications for the analysis of bismuth, but the pharmaceutical and medicinal trades demand a purity of 99·9% and absolute freedom from arsenic.

The following is a typical analysis of market bismuth: silver 0·05, lead 0·005, copper 0·007, iron 0·005, zinc 0·01, bismuth 99·923.

Metallic bismuth is offered for spectroscopical purposes by Messrs. Adam Hilger, Ltd., of a purity of 99·998% (Hilger Publication, No. 94/7, Ap. 1935). E. Matthey, of the firm of Johnson, Matthey & Co., conducted a number of investigations on the refining of the metal, and the methods he proposed for the removal of arsenic, antimony, copper, lead, gold, and silver are as follows:

Arsenic is removed completely by maintaining molten bismuth at a temperature of 510°–520° for some time. There is only a very slight loss due to oxidation.

Antimony is separated by melting the metal and maintaining the temperature at 350°. An alloy of bismuth and antimony, containing over 30% of the latter, rises to the surface of the metal, giving it an " oily " appearance, and can be skimmed off. A complete removal of the antimony is thus effected.

Copper.—For the separation of copper from bismuth which has been previously freed from arsenic, antimony, lead, etc., it is fused with bismuth sulphide. The bismuth sulphide remaining after the fusion and containing copper sulphide may be separated from the bismuth and resmelted. Alkali sulphides may be substituted for the bismuth sulphide in this operation.

Lead may be separated from the fused metal by repeated crystallisations, the alloy of bismuth and lead melting at lower temperatures than bismuth itself. By four crystallisations the percentage of lead has been reduced from 12 to 0·4%.

For the separation of *gold* and *silver* 2% zinc should be added to the molten metal. The mass is gradually cooled and the surface crust removed. This operation is repeated, whereby the whole of the precious metals are concentrated in the skimmings. On fusing these in a crucible with borax, the gold and silver are freed from impurities by the action of the oxide of bismuth, and sink to the bottom. To separate the last traces of these metals from the slag, it is again fused with bismuth.

Sulphur and *arsenic* have received much attention and may be removed by fusion with potassium nitrate with constant stirring at a temperature slightly above the temperature of fusion ; the nitre oxidises the impurities and a little of the bismuth, forming with them a slag which rises and solidifies on the surface. For the complete removal of these impurities a second fusion is frequently necessary.

Sulphur, arsenic, and most of the *antimony* may be eliminated by fusion at a bright red heat under borax, stirring with a rod of iron until the action ceases. The iron combines with the impurities and rises to the surface, from beneath which the still liquid metal may be poured after partial cooling.

Iron may be removed by fusion under a mixture of potassium chlorate and sodium chloride.

Recently patents have been taken out for the refining of metallic bismuth, for example, W. C. Smith specifies that a halogen gas such as chlorine be bubbled through impure bismuth, such as metal containing lead, after which air is bubbled through (U.S.P. 1870388, 1932). Another patent by Smith specifies treatment of the metal at 400° with a current of chlorine under lead chloride or zinc chloride for the removal of lead and zinc respectively.

Properties.—Bismuth is a greyish-white crystalline metal of distinctly red tinge when compared with whiter metals such as zinc or antimony. It is very brittle and easily powdered. Its tenacity is very low. Its hardness is 7·3 on the Brinell scale, decreasing rapidly with increase of temperature even slightly above normal and far below the melting-point. It crystallises in the hexagonal system forming rhombohedra, which approach very closely to the form of cubes. It has also been obtained in the form of acicular needles, which are really elongated hexagonal prisms (Heberdey, Ber. Akad. Wien, 1895, **104**, i, 254). Bismuth has m.p. 271° (Mylius and Groschuff), and b.p. 1490° (O. Ruff and B. Bergdahl). The vapour density at temperatures between 1,600° and 1,700° is 11, which corresponds with that calculated for a mixture of monatomic and diatomic molecules (Meyer, Ber. 1889, **22**, 726). Its sp.gr. at 20° is 9·80, and at the melting-point is 10·067. W. Spring has shown that by the exposure of bismuth of density 9·8 to a pressure of 20,000 atmospheres, the density was raised to 9·856 ; a second compression still further increased the density to 9·863 (Ber. 1883, **16**, 2724). It is stated that by careful hammering its density may be raised to 9·88.

Bismuth expands on cooling after solidification to the extent of 3·32% of the solid volume at the melting-point. The sp.gr. of molten bismuth decreases as the temperature is raised from 10·062 at 275° to 9·611 at 650°.

According to Cohen and Moesveld (Chem. Weekblad, 1913, **10**, 656) bismuth exists in two enantiotropic modifications, the transition temperature being 75°/760 mm., but this transformation has not been confirmed by recent work (Schulze, Z. Metallk. 1930, **22**, 194, 308).

Bismuth is a bad conductor of heat and electricity, its thermal conductivity is 0·018 calorie per second per c.c. per degree at 100°, being less than that of any other metal except mercury. As a conductor of electricity it is even poorer than mercury. For most metals the electrical resistance is roughly doubled when they are melted ; with bismuth it is the reverse, the molten metal being more than twice as good a conductor as the solid. Antimony is the only other metal which shows a decrease in electrical resistance when melted, and in this case the difference is much less marked.

When comparatively pure, bismuth crystallises readily. To obtain it in the form of fine crystals it is melted and allowed to cool until a crust has formed ; the crust is pierced on opposite sides with a hot iron, and the still liquid portion poured through one of the openings. On careful removal of the crust the sides of the vessel are found covered with crystals, frequently resembling hollow pyramidal cubes like those of salt, but which are in reality rhombohedra. Their iridescent lustre is due to a very thin film of oxide which shows the colour characteristic of thin plates.

Bismuth is the most diamagnetic substance known, a bar of the metal placing itself equatorially between the poles of a magnet, *i.e.* at right angles to the position taken up by a bar of iron. When bismuth is placed in a magnetic field it becomes a better conductor of heat. Bismuth also occupies an extreme place in the thermo-electric series, possessing a thermal e.m.f. about 80 micro-volts per degree C. against silver. A junction between pure bismuth and a bismuth alloy containing 5% tin may develop an e.m.f. of about 120 microvolts per degree and a bismuth-tin alloy coupled with copper may yield a difference of 676 microvolts per degree rise in temperature. Bismuth resembles both lead and antimony in its physical and chemical properties. The absorptive powers of bismuth for X-rays are similar to those of lead, and in its chemical reactions it more nearly resembles antimony.

Exposed to dry air, bismuth remains unaltered at the ordinary temperature, but in moist air or in contact with water it becomes coated with oxide. When heated in air it burns with a bluish flame, evolving yellowish fumes of oxide. At high temperatures it decomposes water.

Cold sulphuric acid has no action on bismuth, but it is dissolved by the hot concentrated acid. Hydrochloric acid acts but slowly, and Ditte and

Metzner have shown (Compt. rend. 1892, **115**, 1303) that this action can only take place in presence of oxygen. Nitric acid, dilute or strong, dissolves it readily, with the formation of nitrate. Powdered bismuth thrown into chlorine gas ignites with the formation of trichloride. It also unites directly with bromine, iodine and sulphur.

Analysis.—For the detection and estimation of bismuth, *see* CHEMICAL ANALYSIS.

Uses and Alloys of Bismuth.—Bismuth metal is much too brittle to be used alone on a large scale, but it has been produced as wire in lengths of 20 ft. by extrusion at elevated temperatures. For wire, the liquid metal may also be drawn within glass tubes and allowed to solidify ; after this the glass may be removed by means of hydrofluoric acid, or left in place for insulation and protection. The bismuth wire thus produced has been used in thermopiles, pyrometers, galvanometers, as suspensions and for hair lines in microscopic work. The high thermal e.m.f. of bismuth can be used to produce a very sensitive thermocouple, but the wire is brittle and difficult to handle.

Plates of bismuth metal have been used instead of glass as a surface for certain friction and lubrication tests.

Bismuth has also been used to a small extent for the making of special patterns, owing to the sharpness of the castings produced.

Lead, Tin, and Cadmium Alloys.—The alloys of these metals with bismuth are of special interest. Bismuth acts as a hardening agent and its use has been recommended for this purpose in lead plates for storage batteries. Added to tin, bismuth also imparts hardness sonority and lustre. Bismuth greatly increases the tensile strength of tin from 1·0 ton per sq. in. to 4·5 tons with a bismuth content of 4 to 5%. It also has a profound refining influence on the grain size of tin, producing a much finer grain structure than any other alloying element yet investigated (Hanson and Sandford, J. Inst. Metals, 1925, **56**, 200). In these alloys, however, the chief function is to lower the melting-point, and many of the alloys melt when placed in hot water. Bismuth, when in sufficient quantity, causes expansion on cooling and solidification of alloys used for making casts of insects and other fragile bodies, electrotype moulds, etc. Bismuth also improves the casting properties of lead and tin by reducing the surface tension, thereby producing sharply defined castings even when its percentage is insufficient to cause the metal to expand and fill the mould at the moment of solidification.

The bismuth alloys with low melting-points are known as a class as fusible metals. If bismuth, m.p. 271°, be alloyed in a definite proportion with lead, m.p. 327°, a eutectic mixture is obtained with m.p. 127°, and constitutes the alloy of bismuth and lead with the lowest melting-point. In the same way, if bismuth be alloyed with tin (m.p. 232°) in the eutectic proportion, the resulting alloy will have m.p. 133°. The eutectic alloy of lead and tin has m.p. 182°. By making a ternary eutectic containing bismuth 52·5, lead 32, and tin 15·5, an alloy is obtained with a melting-point below the temperature of boiling water, namely 96°, which is useful for this reason. This is the alloy with the lowest melting-point made from these three metals only, but by adding a fourth metal, namely cadmium, alloys with still lower melting-points are obtained. The quaternary eutectic of these metals, containing bismuth 50·0, lead 28·9, tin 12·25 and cadmium 8·85, has m.p. 70°.

The addition of mercury to any of these alloys will lower the melting-points still further. A number of alloys with low melting-points are put upon the market under the general name of fusible metals, details of which are given in the following table :

Name of Alloy.	Bismuth.	Lead.	Tin.	Cadmium.	m.p.
Newton's .	50	31·25	18·75	—	98°
Rose's . .	50	28	22	—	100°
D'Arcet's .	50	25	25	—	97°
Lichtenberg's	50	30	20	—	98°
Wood's . .	50	25	12·5	12·5	71°
Lipowitz's .	50	27	13	10	71°

These alloys are used in safety plugs for boilers, automatic sprinklers, and other fire protective devices, electrical fuses, low melting-point solders, and tempering baths for tools.

They are used to furnish gas-tight liquid seals for apparatus such as nitriding ovens and also for certain toys, such as "magic teaspoons," which melt in hot water.

Wood's metal has been used for joining the ends of quartz rods and tubes. The quartz is platinised, plated, and tinned, and then inserted into special tinned sockets and the joints made with the alloy.

It is also used for filling thin-walled tubes of brass, copper, etc., which have to be bent into coils or spirals, and for facilitating the bending of other light sections notably in aeroplane construction ; the core prevents collapse and may easily be removed.

Lichtenberg's alloy is used for making metallic writing pencils and similar American pencils contain bismuth 53, lead 42, and mercury 5.

Mercury dissolves a considerable amount of bismuth without solidifying ; the amalgam containing 20% bismuth adheres strongly to smooth surfaces such as glass, and bismuth amalgams with or without tin and lead have been used for the production of mirrors with a lustre reported to be equal to that of silver. The amalgam consisting of one part bismuth and 2 parts mercury is pasty. The amalgam made from 100 parts D'Arcet's alloy and 250 parts mercury is used on account of its low melting-point, for taking casts of anatomical preparations ; the amalgam is introduced in the liquid state, allowed to solidify, and the fleshy parts dissolved by means of a solution of caustic soda.

Bismuth has been used as an addition to Britannia metal and to pewter ; it has also been used as an addition to antimonial lead, the following compositions having been used for stereotype plates: lead 70, antimony 15, bismuth 15, and lead 82, antimony 9, bismuth 9.

An alloy which has been used for hardening bearing metals contains antimony 70, tin 25, copper 3, and bismuth 2%, and a patent has been obtained by J. Geppert (U.S.P. 1584927, 1926) for an antimonial lead alloy containing 2 to 16% bismuth and a little cadmium for bonding glass.

Bismuth in amounts up to 1% has been added to various brasses and bronzes but smaller amounts such as are present as impurity in the copper used are regarded with suspicion.

An investigation has been carried out on the influence of bismuth on the properties of cast iron and steel by E. K. Smith and H. C. Aufderhaar (Iron Age, 1931, **128**, 96). These workers find that quantities of 2% bismuth melted immediately and sank to the bottom of the molten iron or steel. Bismuth was found to act primarily as a deoxidiser and to give fluidity to the molten metal. In the case of cast iron it also acted as a softener, the strength and Brinell hardness being lowered while the machinability is increased somewhat, regardless of the hardness number.

Minute quantities of bismuth in copper or gold render these metals unworkable and its presence in small quantities in lead which is intended for the manufacture of white lead is objectionable, as it leads to a bad colour in the product.

COMPOUNDS OF BISMUTH.

By far the most important uses of bismuth are in the form of its compounds which are extensively used in medicinal and cosmetic preparations. It has been calculated that some 80% of the total bismuth produced is used in pharmaceutical preparations. A number of the compounds are used in treating wounds and these are of special importance in times of war. Insoluble compounds of bismuth are given to patients preparatory to X-ray examination of the stomach and œsophagus. Smaller amounts of bismuth compounds have been used in porcelain painting, in enamelling, and in optical glass manufacture.

Hydride.—A gaseous hydride of bismuth is formed on the solution of an alloy of equal weights of bismuth and magnesium in 4*N*-hydrochloric or sulphuric acid. The hydrogen evolved contains traces of this hydride the presence of which may be established by a mirror test from a Marsh's apparatus, the mirror is similar to that obtained from antimony hydride.

It is fairly stable at ordinary temperatures and is absorbed by water and dilute sulphuric acid to some extent (Paneth, Ber. 1918, **51**, 1704; Paneth and Winternitz, *idem*. **51**, 1728; Paneth, Matthies, and Schmidt-Hebbel, *idem*. 1922, **5** [B], 775).

Oxides.—By far the most important oxide of bismuth is the trioxide, and this together with the compounds derived from it are the only ones of commercial importance. Several other oxides of the metal have been described, including the suboxide, tetroxide, pentoxide, hexoxide, and peroxide.

Bismuth trioxide, Bi_2O_3, occurs in nature as *bismuth ochre*. It is best prepared by heating the basic nitrate until red fumes cease to be evolved. It may also be prepared by exposing the metal to a red-white heat in a muffle. The metal then burns and forms the oxide, which condenses as a yellow powder. Bismuth oxide thus obtained is a pale yellow amorphous substance, *d* 8·21; it melts at 820° to a brown liquid. Heated in sulphur dioxide, it is ultimately converted into a basic sulphate, $4Bi_2O_3,3SO_3$ (D. J. Hammick, J.C.S. 1917, **111**, 379).

The oxide can be obtained crystalline, and has been shown to be isodimorphous with antimony trioxide. It has been used as a catalyst for the oxidation of hydrocyanic acid, and has been added to ferric oxide to form a catalyst for the oxidation of ammonia. Owing to the volatility of the oxide the life of these catalysts at elevated temperatures is short. It is used for glass and porcelain staining; as an addition to certain fluxes to prevent the production of colour, and in gilding porcelain, being mixed in the proportion of 1 part oxide to 15 parts of the gold.

The darkening of the commercial substance on exposure to light is due to the presence of a trace of silver.

A hydrated bismuth oxide, Bi_2O_3,H_2O, is precipitated as a white powder on addition of caustic alkali to a bismuthous salt, such as the nitrate; but Thibault (J. Pharm. Chim. 1900 [vi], **12**, 559) has shown that under these conditions the product contains appreciable quantities of oxy-acid salts. By precipitating the hydroxide from an alkaline solution by the addition of acid, a pure product is obtained which on drying yields the pure oxide. It dissolves in alkali in presence of glycerol.

Basic bismuth carbonate,

$$2(BiO)_2CO_3,H_2O,$$

is best prepared by the addition of ammonium carbonate solution to bismuth nitrate solution. The carbonate separates as a white powder, which is washed and dried at a gentle heat. It is tasteless and stable in air, insoluble in water and in neutral organic solvents. On heating to 100° it loses water, whilst stronger heating converts it into the trioxide. It is used as a medicine and for pharmaceutical purposes, the arsenic limit is 2 parts per million.

Bismuth nitrate, $Bi(NO_3)_3,5H_2O$, is prepared by dissolving bismuth or its oxide or carbonate in moderately strong nitric acid. The concentrated solution is filtered if necessary through asbestos, and deposits on cooling large deliquescent crystals, which are caustic and dissolve in their water of crystallisation when gently heated. On addition of water to the nitrate solution a white precipitate of basic nitrate falls, the constitution of which varies with the amount of water used. This was formerly known as *magistery of bismuth*, and is now called *flake* or *pearl white*, the latter name being also applied to the oxychloride of bismuth.

For pharmaceutical purposes the basic nitrate is prepared as follows: dissolve 2 parts of bismuth in 4 parts nitric acid (*d* 1·42), diluted with 3 parts water, decant from any deposit, evaporate to one-third the bulk, and pour into 80 parts of water, filter, wash and dry the precipitate at a temperature not above 55°.

It is a pearly-white powder consisting of minute crystalline scales. It is employed as a flux for certain enamels, augmenting their fusibility without imparting any colour, and on this account is used as a vehicle for metallic oxides. For the colourless iridescent glaze on porcelain the basic nitrate is rubbed with resin and gently heated with lavender oil ; by the addition of coloured oxides, yellow and other colours are produced. It is also used, like the oxide and in the same proportions, for gilding porcelain, and to some extent as a cosmetic under the names *blanc de fard* and *blanc d'Espagne*. It is largely used in medicine.

Bismuth chloride, $BiCl_3$. This compound is produced when finely powdered bismuth is thrown into chlorine gas or when chlorine is passed over the heated metal. It is also formed by the solution of bismuth in *aqua regia* and evaporation of the liquid, or by distilling a solution of the oxide in hydrochloric acid, changing the receiver when all the water has distilled over.

It is a white solid which melts at 227° and boils at 438°, and absorbs moisture from the air, forming a crystalline hydrate. By the addition of water a white precipitate of basic chloride or oxychloride is produced corresponding to $BiOCl$. Bismuth chloride has been used to render less inflammable some waterproofing materials such as tar, creosote, and non-drying oils.

The oxychloride of bismuth is, however, usually prepared by pouring a solution of the normal nitrate into a dilute solution of common salt, forming oxychloride of bismuth and sodium nitrate.

It is a white pearly powder known as *pearl white*, and is used as a pigment and in the preparation of a very fine yellow pigment known as Merimée's antimony yellow (*v.* ANTIMONY). For double salts of bismuth chloride and chlorides of bivalent metals, *see* Weinland, Alber, and Schweiger, Arch. Pharm. 1916, **254**, 521.

Bismuth iodide, BiI_3. This compound is produced when powdered bismuth is treated with iodine and the product is heated. It is also obtained by precipitating a bismuth salt with potassium iodide solution, dissolving the precipitate in hydriodic acid and reprecipitating with water. The best method of preparation is by the addition of bismuth oxide to a solution of iodine in stannous chloride saturated with hydrochloric acid (Birckenbach, Ber. 1907, **40**, 1404).

Bismuth iodide sublimes in greyish-black, six-sided tablets which are not decomposed by cold water, although they are converted by hot water into an insoluble oxyiodide. Bismuth iodide forms a large number of double salts.

Bismuth sulphite, produced by the action of sulphurous acid on bismuth carbonate, or by double decomposition between a bismuth salt and an alkali sulphite, is a white crystalline powder, and is used in medical practice to check intestinal fermentation, and in cases of worms.

The organic compounds of bismuth have found many applications in medicine and surgery (*see* below).

A general method for the preparation of bismuth salts of organic acids is the solution of freshly precipitated bismuth hydroxide in a solution of the acid (Fischer and Grützner, Arch. Pharm. 1894, **232**, 460 ; *v. also* Telle, *ibid.* 1908, **246**, 484, for the preparation of *bismuth lactate* by this method).

Bismuth salicylate is prepared by the interactions of solutions of bismuth nitrate and sodium salicylate. Hydrated bismuth salicylate $Bi(C_7H_5O_3)_3,4H_2O$, is thus obtained as a white powder, insoluble in cold water and stable in air, but it must be protected from light.

Martinotti and Cornelio (Boll. Chim. farm. 1901, **40**, 141) point out that commercial preparations of the salt vary very much in composition, the amount of acid ranging from 5 to 67%, and that of bismuth oxide from 37 to 79%.

Thioform, bismuth dithiosalicylate, used as a substitute for iodoform (*v.* SYNTHETIC DRUGS).

Emetine and bismuth iodide is a complex iodide of bismuth, and may be prepared by precipitation from a solution of emetine hydrochloride by the addition of a solution of potassium bismuth iodide. It contains not less than 25 and not more than 28% of emetine, $C_{29}H_{40}O_4N_2$, and not less than 18 or more than 21% bismuth. It is a reddish-orange powder, odourless, but with a bitter and acrid taste. It is insoluble in water or alcohol but soluble in acetone. It is insoluble in dilute acids, but undergoes slight decomposition in these and is soluble with decomposition in concentrated acids and in alkaline solutions. It should be kept away from light (Brit. Pharm. 1932, 147).

Basic bismuth gallate, known commercially as *dermatol*, is prepared by treating a solution of bismuth nitrate in nitric acid with a solution of gallic acid in 70% alcohol, nearly neutralising with sodium hydroxide or sodium carbonate, and finally adding considerable quantities of sodium acetate or diluting largely with water. The compound is thus obtained as a yellow precipitate, which is collected and dried (E.P. 6234, 1891).

The empirical formula of the substance is $BiC_7H_7O_7$, and Thibault (J. Pharm. Chim. 1901, [vi], **14**, 487) considers that it is really bismuthogallic acid, adducing in favour of this view the fact that with alkalis it forms salts of which potassium bismuthogallate, $K_2BiC_7H_5O_7$, is a type.

Bismuth hydroxyiodogallate,

$$C_6H_2(OH)_3{\cdot}CO_2{\cdot}BiI(OH),$$

airol, is prepared by heating together in 50 parts of water 35 parts bismuth oxyiodide and 18·8 parts gallic acid until the product is a greyish-green powder. It is used as a substitute for iodoform.

Other compounds of bismuth to which trade names have been given are :

Markasol, bismuth borophenate.

Bismal, bismuth methylenedigallate, obtained by the general method from the hydroxide and methylenedigallic acid.

Basic bismuth dibromohydroxynaphthoate, which has been suggested as a substitute for iodoform in surgical dressings (G. Richter, Apoth.-Ztg. 1908, **23**, 600), is obtained by a similar method. β-Hydroxynaphthoic acid is brominated in acetic acid solution, and the recrystallised product heated with bismuth hydroxide. The salt is a finely crystalline, yellow, odourless, insoluble powder, which is unaffected by heating to 110°.

Bismuth chrysophanate (*Dermol*),

$$Bi(C_{15}H_9O_4)_3 \cdot Bi_2O_3(?),$$

a yellowish-brown powder, is, according to Merck, a mixture of impure chrysarobin and bismuth hydrate.

Compounds of bismuth with phenols are obtained by double decomposition between an alkaline salt of the phenol and a salt of bismuth, such as the nitrate. Among those that have been made commercially may be mentioned:

orphol (the β-naphthol compound),

$$C_{10}H_7OBi(OH)_2 + Bi_2O_3 + H_2O\,;$$

xeroform (the tribromophenol compound),

$$(C_6H_2Br_3O)_2BiOH + Bi_2O_3\,;$$

helcosol (the pyrogallate),

$$[C_6H_3(OH)_2O]_2 \cdot Bi \cdot OH.$$

An important pathological application of bismuth salts is their administration internally in order to outline parts of the body in X-ray work. C. O. B.

Organic Compounds of Bismuth.

The organic derivatives of bismuth may be divided into two main classes : (1) the organo-compounds, which contain a carbon-bismuth linkage, are not ionised, are very reactive, and possess many properties of considerable theoretical interest ; (2) the salts, both neutral and basic, which the metal forms with organic acids, some of which, especially those containing the bismuthyl radical —**BiO**, have found application in the treatment of spirochæte infections.

(1) The organo-compounds may be prepared according to two principal methods from the anhydrous metal halides. The older dating from 1850, consists in the interaction of the halide with the alkyl- or aryl- derivatives of zinc or mercury (ZnR_2 or HgR_2). The other method is a modification of this in which a magnesium alkyl or aryl halide is used (Ber. 1904, **37**, 4620).

$$2BiX_3 + 3ZnR_2 = 2BiR_3 + 3ZnX_2$$
$$BiX_3 + 3MgRX = BiR_3 + 3MgX_2$$

In this way numerous tertiary alkyl- and aryl-bismuthines have been prepared (J.C.S. 1914, **105**, 2210 ; 1922, **121**, 104, where numerous references are given) but primary and secondary bismuthines $BiRH_2$ and BiR_2H are unknown. The trialkylbismuthines are colourless or pale yellow liquids, miscible with most organic solvents, often spontaneously inflammable in air, and having a very unpleasant odour. The triarylbismuthines, on the other hand, are crystalline solids, which are stable in air and odourless. Strong acids decompose them, liberating the hydrocarbon, thus :

$$BiR_3 + 3HCl = BiCl_3 + 3RH$$

Tri*cyclo*hexylbismuthine, however, resembles the alkyl- rather than the arylbismuthines (Ber. 1914, **47**, 3257). The tertiary arylbismuthines combine with chlorine and bromine to form well-crystallised addition products, the triarylbismuthine dihalides, R_3BiX_2 (Annalen, 1889, **251**, 323). These are stable to acids but break down at or below 100° giving aryl halide and diarylhalogenbismuthine. Tertiary bismuthine and aryldihalogenbismuthine are sometimes produced in this reaction,

$$(1)\ R_3BiX_2 = R_2BiX + RX\,;$$
$$(2)\ 2R_3BiX_2 = R_3Bi + RBiX_2 + 2RX$$

The tendency of bismuth to assume the quinquevalent condition, which is but feebly developed in the inorganic compounds of this element, is brought very strongly to light by the formation of R_3BiX_2.

Triarylbismuthine di-iodides are unknown (J.C.S. 1924, **125**, 855), addition of iodine causing immediate elimination of aryl iodide, except at about −70°, at which temperature the di-iodide is probably stable: $R_3Bi + I_2 = R_2BiI + RI$. This last type of reaction is general for the trialkylbismuthines (Ber. 1887, **20**, 1516, 1888), the dihalides of which have not been prepared, *e.g.*

$$(C_nH_{2n+1})_3Bi + Br_2 = (C_nH_{2n+1})_2BiBr + C_nH_{2n+1}Br$$

The alkyl- and arylhalogenbismuthines $RBiX_2$ and R_2BiX may be prepared in a more convenient manner by a method (Annalen, 1889, **251**, 328) which is of general application to most organometallic compounds—the interaction of ethereal solutions of a tertiary bismuthine and bismuth halide :

$$2R_3Bi + BiX_3 = 3R_2BiX\,;$$
$$R_3Bi + 2BiX_3 = 3RBiX_2$$

The analogous reactions in the cases of tin, antimony, and arsenic require heat.

The properties of the arylhalogenbismuthines are in striking contrast with those of the bismuthine dihalides. As would be expected from their close relation to the tertiary bismuthines, they are readily decomposed by acid giving bismuth salts and a hydrocarbon (this property affords a ready means of determining the metal in organo-derivatives of tervalent bismuth). They are also, like the bismuth halides, decomposed by water, thus :

$$R_2BiX + H_2O = 2RH + BiOX$$

With alkalis they yield bismuth hydroxide and the bismuthine, reacting in this respect as $xBiR_3 \cdot yBiX_3$. Towards many aryl- or alkyl-magnesium halides they behave similarly, *e.g.* **MgEtBr** with diphenylbromobismuthine gives triphenyl and triethyl-bismuthines (J.C.S. 1914, **105**, 2216 ; 1921, **119**, 922), and a number of other examples of this type of reaction have been described (J.C.S. 1921, **119**, 920).

On the other hand, with magnesium α-naphthyl bromide, diphenylbromobismuthine gives diphenyl-α-naphthylbismuthine,

$$Ph_2Bi \cdot C_{10}H_7,$$

m.p. 118°–119°, the only mixed bismuthine so far described (J.C.S. 1914, **105**, 2216). Possibly reaction with the Grignard reagent under carefully controlled conditions might lead to the isolation of other derivatives of this type which, however, on analogy with the mixed mercury aryls and alkyls, would probably readily decompose to the symmetrical compounds.

The ready transfer of hydrocarbon groups from zinc, mercury, or magnesium which is observed in the reactions of the organo-derivatives of these elements, and which is so important in the synthesis of other organo-metallic compounds, is not to be regarded as characteristic of these elements only but is exhibited by other electropositive metals such as lead, tin, and bismuth. Thus triphenylbismuthine reacts with phosphorus trichloride, boron tribromide and arsenic trichloride giving diphenylchlorobismuthine or diphenylbromobismuthine and phenyldichlorophosphine, $C_6H_5PCl_2$, phenyl boron dibromide, $C_6H_5BBr_2$, and phenyldichloroarsine, $C_6H_5AsCl_2$ respectively. Many other reactions of this type are known (J.C.S. 1924, **125**, 864).

Further properties of the triarylbismuthine dihalides.—Birckenbach and Kellermann (Ber. 1925, **58** [B], 786, 2377) from a study of the decomposition potentials of the potassium halides and the analogous salts of those radicals which resemble the halogens (the so-called pseudohalogens) arranged these elements and radicals in the series F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN.

The relative stability of the triphenylbismuthine dihalides and dipseudohalides, Ph_3BiX_2, as indicated by the ease of elimination of C_6H_5X follows the same order, the most stable being the difluoride (m.p. 159°, J.C.S. 1922, **121**, 91) and dicyanate (m.p. 128°–129°, J.C.S. 1927, 209), whereas the di-iodide (*see* above), dithiocyanate, and diselenocyanate (J.C.S. 1922, **121**, 91 ; 1926, 1651) decompose immediately according to the general equation. Further, the dichloride and diazide are of about the same degree of stability, eliminating chlorobenzene and phenylazide at about 110° (J.C.S. 1934, 408).

Mixed dihalides of the type R_3BiXY, where X and Y are different halogens, have not been obtained. Interaction of triphenylbismuthine with iodine bromide or chloride or with cyanogen iodide gives in each case iodobenzene and the corresponding diphenylhalogen (pseudohalogen) bismuthine:

$$Ph_3Bi + IX = PhI + Ph_2BiX$$

The more electropositive halogen is eliminated in union with phenyl (J.C.S. 1915, **107**, 16). With cyanogen bromide and chloride the same regularity obtains, but in accordance with the position of chlorine, bromine, and cyanogen in the electrochemical series of Birckenbach and Kellerman (*see* above) the products are benzonitrile with diphenylbromobismuthine and diphenylchlorobismuthine (J.C.S. 1924, **125**, 259).

Triphenylbismuthine dihydroxide is obtained in aqueous solution by shaking the dichloride with silver oxide and water. Treatment of this solution with dilute halogen acids or with sodium halides precipitates the hydroxyhalides $Ph_3Bi(OH)X$. Concentration of the aqueous hydroxide solution at 100° gives only triphenylbismuthine, but slow evaporation at 40° under diminished pressure yields the dihydroxide or oxide as a white solid which readily decomposes in organic solvents (J.C.S. 1934, 407).

Nitro derivatives of triphenylbismuthine dinitrate.—Owing to its instability to nitric and sulphuric acids triphenylbismuthine itself has not been directly nitrated (the statement of Gillmeister, Ber. 1897, **30**, 2844) that *o*-dinitrobenzene is obtained on treatment with nitric and sulphuric acids could not be confirmed) but triphenylbismuthine dinitrate readily yields a number of nitro derivatives, of which the tetranitro- compound has been most studied (J.C.S. 1924, **125**, 862). The tetranitro- derivative on conversion to the dichloride, m.p. 146°, and gently heating, gives *m*-chloronitrobenzene. The nitro group therefore enters the molecule in the *m*-position to the $\geqslant Bi(NO_3)_2$ group. The results of a quantitative study of the nitration of triphenylbismuthine dinitrate (J.C.S. 1934, 1258) reveal the formation of 86% of *m*-nitro compound.

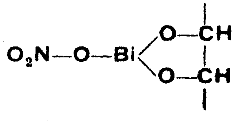
(II) The organic salts of bismuth which find application in the treatment of spirochæte and similar infections are either basic bismuth salts or bismuthyl (-BiO) derivatives. True organo-compounds analogous to atoxyl or salvarsan have not been prepared.

Rosenheim and Vogelsang (Z. angew. Chem. 1906, **48**, 205) studied the interaction of bismuth salts with tartaric acid, and obtained potassium monobismuthyl tartrate (the analogue of tartar emetic). An oil suspension of this compound has been employed in many cases of syphilis. These authors also describe a potassium tribismuthyl tartrate. Maschman (Arch. Pharm. 1925, **263**, 101) gives references to the pharmacological properties of these compounds and describes the preparation of crystalline sodium tribismuthyl tartrate

$$NaOOC{\cdot}CHO(BiO){\cdot}CHO(BiO){\cdot}CO{\cdot}O(BiO),2H_2O$$

from sodium tartrate and an acidified bismuth nitrate solution. The E.P. 258641 deals with compounds of bismuthyltartaric acid and bases such as diethylamine, piperazine, and hexamethylenetetramine, and refers to their therapeutic possibilities.

Bismuth nitrate also reacts with polyhydroxy-compounds such as mannose, fructose, and xylose, giving clear solutions from which alcohol precipitates compounds in which the bismuth atom appears to be linked thus:



probably to carbon atoms 2 and 3 in the sugar. The mannose and fructose derivatives are soluble in water and have the composition $C_6H_{10}O_6{\cdot}BiNO_3$. Mannitol and erythritol give similar compounds $C_6H_{12}O_6{\cdot}BiNO_3$ and $C_4H_8O_4{\cdot}BiNO_3$.

Maschman (*ibid.* 721) has prepared certain bismuth and bismuthyl salts of aromatic arsonic acids by interaction of fructose-bismuth nitrate with the sodium salts of the acids, *e.g.* the basic bismuth salt of 3-amino-4-hydroxyphenylarsonic acid. Levaditi, who has carried out much work at the Pasteur Institute on spirillocidal compounds, describes the corresponding acetyl derivative (F.P. 609146). The G.P. 414799 describes various arsenical bismuth compounds obtained by adding bismuth trichloride or the bismuth compounds of sugars or polyhydric alcohols to salvarsan hydrochloride or its derivatives, precipitating with sulphuric acid and treating with sodium hydroxide. These substances are stated to be very toxic to *Spirochæta pallida*. Similarly, the F.P. 617063 deals with a compound obtained by dissolving bismuth hydroxide in mannitol solution, adding salvarsan base and precipitating by alcohol. The B.P. 357061 describes compounds obtained by addition of bismuth chloride or nitrate to the sodium salts of aromatic arsonic-stibonic acids, *e.g.* 4-hydroxybenzene-3-stibonic-1-arsonic acid. The compounds are stated to be superior to the usual bismuth compounds for the treatment of syphilis in rabbits.

It is not clear to what extent many of these substances have found permanent use in chemotherapy. F. C.

BISMUTHINITE or **BISMUTH-GLANCE.** Native bismuth sulphide, Bi_2S_3, occurring as acicular or bladed orthorhombic crystals or lamellar masses, very like stibnite (Sb_2S_3) in appearance. In Queensland and Bolivia it is found in sufficient abundance to be mined as an ore of bismuth. L. J. S.

BISMUTHOIDOL "ROBIN." Colloidal metallic bismuth in concentrated, isotonic, sterile aqueous solution. Antiluetic.

BISMUTITE. Basic bismuth carbonate, containing about 90% Bi_2O_3; formula perhaps $Bi_2O_3 \cdot CO_2 \cdot H_2O$. It is a yellowish earthy material, and presenting such an appearance is surprisingly heavy (sp.gr. variously given as 6·9 and 7·6). It occurs as an alteration product of native bismuth and of bismuthinite, and in Bolivia is an important ore of bismuth. L. J. S.

BISMUTOSE. Compound of bismuth 22% and albumin 66%. Antacid. Intestinal astringent.

BISMUTOTANTALITE. Tantalate (and niobate) of bismuth, $Bi_2O_3(Ta,Nb)_2O_5$, occurs as large, rough orthorhombic crystals up to several pounds in weight. It is pitch-black with sub-metallic lustre; sp.gr. 8·03–8·44, H. 5–5½, and is not attacked by acids, including HF. Analyses give Bi_2O_3 50–52, Ta_2O_5 31–41, Nb_2O_5 6–14%. It is isomorphous with stibiotantalite [$(SbO)_2Ta_2O_6$] and tantalite [$FeTa_2O_6$]. It has been found in some abundance in a pegmatite vein on Gamba Hill in Busiro County, Uganda (E. J. Wayland and L. J. Spencer, Min. Mag. 1929, 22, 185). L. J. S.

BISOCOL, an antiluetic, containing 20–25% colloidal metallic bismuth. Forms brilliant black non-hygroscopic scales, readily soluble in water.

BISTOVAL, the bismuth salt of acetarsol (*v.* ARSENICALS, ORGANIC).

BISTRE. Brownish-black soot obtained chiefly from the smoke of beech wood. Is sometimes used as a pigment.

BITTER APPLE. *Syn.* for Colocynth, *q.v.*

BITTER-SWEET. *Syn.* for Dulcamara, *q.v.*

BITTER-WOOD. *Syn.* for Quassia, *q.v.*

BITTERN. The mother liquor which remains after the crystallisation of common salt from sea-water, or the water from salt springs. It contains soluble magnesium salts, bromides and iodides. The same term is also applied to a mixture of equal parts of quassia extract and other drugs, formerly used to sophisticate beers.

BITUMEN *v.* ASPHALT and BITUMEN.

BITUMINOUS PLASTICS. Bituminous moulding compositions are used on a large scale for manufacturing battery boxes for motor cars, electrical insulators, and certain small objects formerly moulded from the more expensive shellac moulding materials. These compositions usually contain, in addition to hard asphalts, waxes such as Ozokerite or Montan wax, gums such as Colophony, Congo Copal, Kauri Copal, or Dammar, and fillers such as whiting, silica flour, fibrous asbestos, or cotton linters.

Generally these compositions are manufactured by the firms who mould them, as they are simply made. The constituents are mixed together in a heated mixer, the product is sheeted between rollers and cut up or stamped into conveniently sized pieces for moulding. The material is then pressed into the desired shape in heated moulds operated by hydraulic presses. The mouldings harden on cooling.

In the cold moulding process solvents are included in the composition, which is then plastic at ordinary temperatures and moulded without heat. The moulded objects are stoved to harden them. This hardening is brought about partly by loss of solvent and partly by a polymerisation process.

Although bituminous moulding compositions are generally made by the moulders, some are marketed under such names as "Tenacit," "Telenduron," "Kalanite," and "Stocko."

Asphalt paving materials may be regarded as plastics. They are sometimes known as bituminous concrete. A sort of bituminous macadam was used in the construction of highways by the Incas of Peru, but in modern times asphalt paving was first used in Paris, 1835 (Abraham, "Asphalts and Allied Substances," 3rd ed.). In the construction of roads and pavements material for the base course consists of a coarse mineral aggregate bonded with 4% to 6% bituminous material. Material for the surface course consists of a finer mineral aggregate bonded with 9% to 12% bituminous material. It is applied hot, levelled with a spade, and rolled or tamped to consolidate it.

E. E. W.

BIXA SEED *v.* ANNATTO SEED.

BIXIN, *see* under ANNATTO.

END OF THE FIRST VOLUME.